# INORGANIC AND THEORETICAL CHEMISTRY

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ORGANIC CHEMISTRY

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THE WORLD OF SCIENCE

GENERAL SCIENCE FOR SCHOOLS

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THE CENTURY OF SCIENCE

SCIENCE PAST AND PRESENT

AN ILLUSTRATED HISTORY OF SCIENCE

THE ALCHEMISTS

A HISTORY OF INDUSTRIAL CHEMISTRY

# INORGANIC AND THEORETICAL CHEMISTRY

BY

F. SHERWOOD TAYLOR

Ph.D., M.A., B.Sc.

B. Sc.

*NINTH EDITION*

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# PREFACE

THE purpose of this work is to present within a reasonable compass the facts and principles needed for a sound foundation in Inorganic Chemistry. The book contains two concurrent courses. The matter in larger type is that which an intelligent student might be expected to study in his first year or eighteen months after matriculation ; the matter in smaller type is supplementary to this and is required by the University Scholarship candidate and second-year University student.

The book is arranged in accordance with the Periodic Table. Copious cross-references enable any other order to be taken if preferred. The first eight chapters deal with the fundamental principles of chemistry and with the Physical Chemistry required for an understanding of an inorganic course. These are not intended to present a complete student's course of Physical Chemistry, but rather to afford a ready means of reference to an explanation of the theory of such common phenomena as hydrolysis, reversible reactions, fractional distillation—to name a few of the topics dealt with.

I wish to express my gratitude to Dr. Charles Singer for his kindness in reading the manuscript of the first chapter of the book. My thanks are also due to Dr. F. M. Brewer and Mr. J. T. Lemon, who have given me most valuable advice and assistance ; to Mr. H. Pocock, laboratory assistant at Repton School, to whom I owe the photographs reproduced as Plates XII. and XIV. ; to Messrs. Electrolux, Ltd., and to the British Oxygen Co., for valuable information and for permission to use diagrams ; to Mr. H. Wren, who redrew the majority of the line illustrations, and to Mr. G. Mackay, of the Royal Geographical Society, for the maps which appear as endpapers ; and to the following for kind permission to reproduce illustrations, etc. :—

The Director of the Natural History Museum, South Kensington, for Plates IV.–IX. and XIV.–XVI.

The *Mineralogical Magazine*, for Plate XI.

The Trustees of the Ashmolean Museum, for Plate I.

Dr. P. M. S. Blackett and Messrs. George Bell & Sons, Ltd., for Plate XX.

Messrs. Charles Griffin & Co., Ltd., for Plates XVII.–XIX., from Roberts-Austen's *Introduction to the Study of Metallurgy*.

The Chemical Society, for the Revised Table of Atomic Weights appearing on pp. 176–177 and 829.

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Messrs. Griffin & Tatlock, for Fig. 91.

Messrs. Longmans, Green & Co., Ltd., for Figs. 120, 121 and 153, from Thorpe's *Dictionary of Applied Chemistry*, and Fig. 11, Vol. X., from Mellor's *Comprehensive Treatise of Inorganic and Theoretical Chemistry*.

Messrs. John Murray, for Fig. 200, from Russell's *Chemistry of Radio-Active Substances*.

The Society for the Promotion of Hellenic Studies, for Figs. 1 and 2.

The Journal of the American Chemical Society, for Fig. 172.

## PREFACE TO THE SECOND EDITION

In presenting a second edition of this work, the author wishes to acknowledge with gratitude the assistance of numerous correspondents who have pointed out slips and numerical errors, which had escaped his notice in reading the proofs of the first edition. It is hoped that the correction of these will give the book an additional value.

F. S. T.

## PREFACE TO THE THIRD EDITION

ALTHOUGH only four years have passed since the first appearance of this work, the progress in Inorganic Chemistry has been such as to render necessary many additions and alterations.

Not only has new and important knowledge been added to the Science, but the progress of time has rendered so much more prominent certain theoretical aspects that greater emphasis has had to be laid upon them.

It is hoped that the usefulness of the book has been increased without taking away from its clearness of treatment.

F. S. T.

QUEEN MARY COLLEGE,
UNIVERSITY OF LONDON, 1935.

## PREFACE TO THE FOURTH EDITION

THE opportunity has been taken to add notes on a few new developments, among which may be mentioned the structure of the carbonyls, the softening of water by metaphosphates, and the composition of bleaching powder; new work on rhenium and protoactinium, and on certain new compounds such as nitrogen trioxide, sulphur tetroxide, and argentic fluoride.

F. S. T.

QUEEN MARY COLLEGE,
UNIVERSITY OF LONDON, 1938.

## PREFACE TO THE FIFTH EDITION

IN this, the fifth edition, the accounts of industrial processes have been revised, in order to bring them as nearly as possible into conformity with modern practice. The theory of the complete dissociation of strong electrolytes has also been adopted in the theoretical portion of the work.

F. S. T.

## PREFACE TO THE SIXTH EDITION

THE resetting of this book has afforded the opportunity for an extensive revision and the incorporation of such of the conclusions of recent researches as appeared to the author to be significant for the student.

F. S. T.

OLD ASHMOLEAN BUILDING,
BROAD STREET, OXFORD.

## PREFACE TO THE SEVENTH EDITION

MY special thanks are due to Mr. W. M. Hampton of Messrs. Chance Brothers Ltd., for information concerning modern methods of glass manufacture, and to Professor W. E. S. Turner for the loan of the block for Fig. 121.

F. S. T.

OLD ASHMOLEAN BUILDING,
BROAD STREET, OXFORD.

## PREFACE TO THE EIGHTH EDITION
*(Second Impression)*

THE war has brought about many developments in chemical technique, which it is hoped may be included in a later edition. Sections on the transuranic elements and the utilisation of atomic energy have, however, been added to the final chapter. My thanks are due to Mr. E. Dickinson, for reading the proofs and making many valuable suggestions.

F. S. T.

OLD ASHMOLEAN BUILDING,
BROAD STREET, OXFORD, 1947.

## PREFACE TO THE NINTH EDITION

IN this edition the sections dealing with industrial processes have been revised and especial notice has been given to the great advances in metallurgy which have been effected in recent years.

F. S. T.

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# INORGANIC AND THEORETICAL CHEMISTRY

## CHAPTER I

## THE EARLY HISTORY AND METHOD OF CHEMICAL SCIENCE

### CHEMISTRY AS A BRANCH OF NATURAL SCIENCE

**1. The Meaning of Science**

NATURAL science is the process and result of systematically arranging and classifying man's knowledge of the world about him. Each of us in his everyday life and in his profession observes a vast number of facts; that is to say, he receives a great number of impressions on his senses of sight, hearing, touch, etc.; these he stores in his memory and they form his stock of knowledge. The accumulation of facts collected in books and in the minds of men constitutes *knowledge*, but by no means necessarily *science*. Many who are not chemists have a considerable knowledge of chemical facts; they know that sulphur is yellow, that salt is insoluble in benzene, that phosphorus poisons rats, that sodium burns in chlorine forming common salt, and so forth. Just as bricks are not a house, so these isolated facts are neither Chemistry nor Natural Science. None the less, as a house cannot be built without bricks, so a science cannot be constructed except on a basis of facts.

The first step in the formation of a science is the collection of undoubted facts relating to its subject. At this point the philosophers often raise difficulties.

Certain schools of philosophy say with reason that we cannot have any real knowledge of what a *material thing* is like or how it behaves, because the impressions on our senses from which we construct our knowledge are influenced by the nature of our organs of sense. Thus we all agree that sulphur is yellow, and it is exceedingly probable that sulphur looks much the same to all of us, since as far as we can tell we all have the same kind of eyes and brain. But suppose a million Martians with a totally new kind of eye came to the earth; we should hardly expect them to get the same eye



College.

sensation from the sulphur. Who could decide what colour sulphur was if we thought it yellow and these Martians thought it something different? Clearly then we do not know what sulphur, the *thing in itself*, is like or even whether it really exists at all. We only know what effects it has on our senses.

None the less, this last is the thing that matters. For practical purposes we want to know what sulphur seems to be like and not what it is really like. It is only when we get to fundamental questions like the properties of four-dimensional space-time and the behaviour of electrons that we begin to feel that certain things, which appear to us to be true because they 'work,' are inconceivable through the imperfection of our senses. The knowledge that our 'facts' are founded on perceptions, which must themselves be influenced by the eye which perceives or brain which registers, makes us rely for the ground-work of science on the kind of perception which is as little as possible influenced in this way. A measurement with a balance, thermometer, scale, galvanometer, etc., depends only on the perception that two objects (*e.g.*, a pointer and a mark on a scale) coincide. Consequently such measurements vary very little with the observer. If the fact to be observed is a perception of colour or smell, much more doubt is introduced. The relative brightness of two sources of light, as in a photometer, is a matter over which two observers will differ. Modern science, however, has invented an 'electric eye' [1] in which the light causes a current to flow proportional to its intensity, which current is read off on a galvanometer scale. The tendency of science is to reduce all measurements to such as may be read off on a scale, thus eliminating differences between observers.

A mass of facts, however reliable, is not a science. The *Natural History* of Pliny (*c.* 70 A.D.) contains a great accumulation of facts about natural phenomena, but contains no science, for the knowledge it embodies is lacking in any reasoned arrangement. It is only when facts are linked together by ideas, theories and natural laws, in such a way that they can be looked at as a whole and can take their place in the vast pattern of Nature, that a science is formed.

## 2. The Methods of Science

How, then, is a science to be built up? Facts are first collected and *their reliability is ascertained.* The science of ancient times and of the Middle Ages was greatly hampered by lack of this latter precaution. Assertions were handed down, and, even if they were

[1] Consisting of a piece of metal, such as rubidium, fixed in a vacuum tube furnished with electrodes. Light, shining on the metal, causes it to emit ions which carry a current proportional to their number.

not always believed, no attempt was made to rely only on those facts which could be tested. Probably, even in the Middle Ages, few people believed the story that the eagle was so hot that it cooked its own eggs by sitting on them, unless it had taken the precaution of placing in its nest the stone aëtites, which was very cold by nature. None the less, serious authors reported the story and handed it on in succession. Our complaint should not be that people did not reject this story as improbable, for many genuine facts might seem even less probable. The mediæval philosophers would not have gained by mere disbelief. Doubtless, such stories were, in fact, rejected by many sensible people, but the regrettable fact remained that knowledge was not tested by *seeing for oneself*.

To-day a problem is investigated by observation and especially by observation in specially controlled conditions, to which we give the name of experiment. If a man of science makes a set of observations which seem to him to be new and important, he tries to discover from them some common principle which he terms a rule or law. A law is a statement about his observations which he expects to apply to all future observations of the same kind. Graham's Law of Diffusion (§53) may serve as an example. The scientist then publishes his work giving every detail which will enable his fellow-workers to test its truth. On these facts and laws he usually founds a hypothesis; that is to say he makes certain assumptions about what he cannot observe in order to explain the facts he has observed and the laws he has deduced. Thus Graham's law and a great many other laws are explained by the assumptions that gases consist of minute elastic particles in chaotic motion. These assumptions are called a hypothesis, theorem or theory, the latter words being usually applied to assumptions that appear to be very well founded. If other men of science are interested in the work, they will repeat it and so test the facts for themselves. The hypothesis is next tested by using it to *predict* what will happen under certain conditions which can be produced experimentally. If actual experiments then show that these predictions are correct, the belief that the hypothesis represents a scientific truth is confirmed though it cannot be fully proven.

In time, if the hypothesis survives these tests, it is dignified by the name of a Theory and forms an important part of the fabric of the science. It remains, however, a theory until it can be proved by observation to be fact, when it can rank as a law, i.e., a direct induction from observations. As an example we may take the belief, put forward by Avogadro and founded on a series of facts connected with the volumes and weights of gases, that "equal volumes of gases contain equal numbers of molecules under the same

conditions of temperature and pressure." For many years, while the defects in atomic weights hindered the perception of its value, chemists rightly spoke of Avogadro's *hypothesis*; then, as its remarkable power of accounting for and predicting facts became clear, they termed it Avogadro's *Theorem* ; and finally, now that actual physical experiment has enabled us to count molecules and so to prove its truth to the hilt, we speak of Avogadro's *Law*.

A hypothesis is a guess or deduction, which, if true, will account for a set of facts. A theory is a hypothesis which is apparently well confirmed, and a law is a concise statement covering a wide range of facts and so well confirmed as to be practically beyond doubt.

There is, of course, a complete dissimilarity between the legal and the scientific uses of the word ' law.' A law in the legal sense is a rule of conduct laid down by a powerful intelligent being or group of beings as a guide which the less powerful are compelled by their sense of duty, shame or fear to obey. A scientific law is a statement that certain phenomena have occurred in a certain way so often that it is extremely probable that they will continue to do so. The use of the word ' law ' does not imply that natural phenomena *must* obey natural laws. An apple does not fall because it has a respect for the law of gravitation, which indeed exists only in the minds of men.

## 3. The Divisions of Natural Science

Natural science forms a coherent whole, but is artificially divided into departments for the purpose of study. The chief departments of Natural Science are the following :—

1. PHYSICS, which deals with the properties common to matter in general and with the various manifestations of energy and their transformations.
2. CHEMISTRY, which deals with the composition and properties of the different kinds of matter.
3. BIOLOGY, which is concerned with the phenomena peculiar to living things.
4. ASTRONOMY, which deals with the structure and motions of the universe and the chemistry and physics of matter outside our planet.
5. GEOGRAPHY and GEOLOGY, which deal with the structure of the earth.

All the minor sciences fall under one or more of these headings. Mathematics and Logic are not to be considered as sciences, but rather as methods of classifying and investigating the facts presented by other sciences.

## 4. Chemistry before the Arabs

Chemistry as a science is but a modern growth. Before the seventeenth century of the Christian era it can hardly be said that any effective and systematic attempt had been made to study the properties and constitution of matter. Yet, although Chemistry as a science is but recent, Chemistry as a craft is of great antiquity. Chemical operations, distillation, evaporation, crystallisation, filtration, precipitation and the preparation of substances in a state of purity, were used in technical processes and in the pseudo-science of Alchemy, long before the science of Chemistry came into being.

It is impossible to say where and when the chemists' craft began. The compounder of drugs, found in most primitive communities, has since the remotest times practised a simple kind of chemistry, purifying and concentrating the active principles of plants by extraction with boiling water, filtration through cloths and evaporation. The primitive worker in metals, too, practises a crude type of chemistry in his processes for extraction and purification of metals.

As communities became more civilised, so the chemist's craft became more complex and varied. In Egypt and Assyria between, say, 4000 and 600 B.C., such arts as metal-working, painting, dyeing, enamelling, glass-making, pharmacy and the like, led to the use of a great variety of materials. These crafts were further developed in the Greek and Roman civilisations.

In Pliny's famous *Natural History*, written about 70 A.D., we find a great many practical chemical processes described. The metals, their ores and simple products, and such salts as soda, common salt, alum, iron sulphate, white lead, copper sulphate, are clearly described and the methods of preparing them are explained. The work is, however, essentially a description of the industries carried on by the Romans and makes no attempt to set apart chemistry as an art or science.

Perhaps we may find the earliest trace of anything allied to a science of chemistry in the works of the Greek philosophers. Such men as Thales, Democritus and Aristotle were in no way practical chemists, but they attempted to form an idea of the nature of matter by considering such phenomena as evaporation, putrefaction, growth and decay.

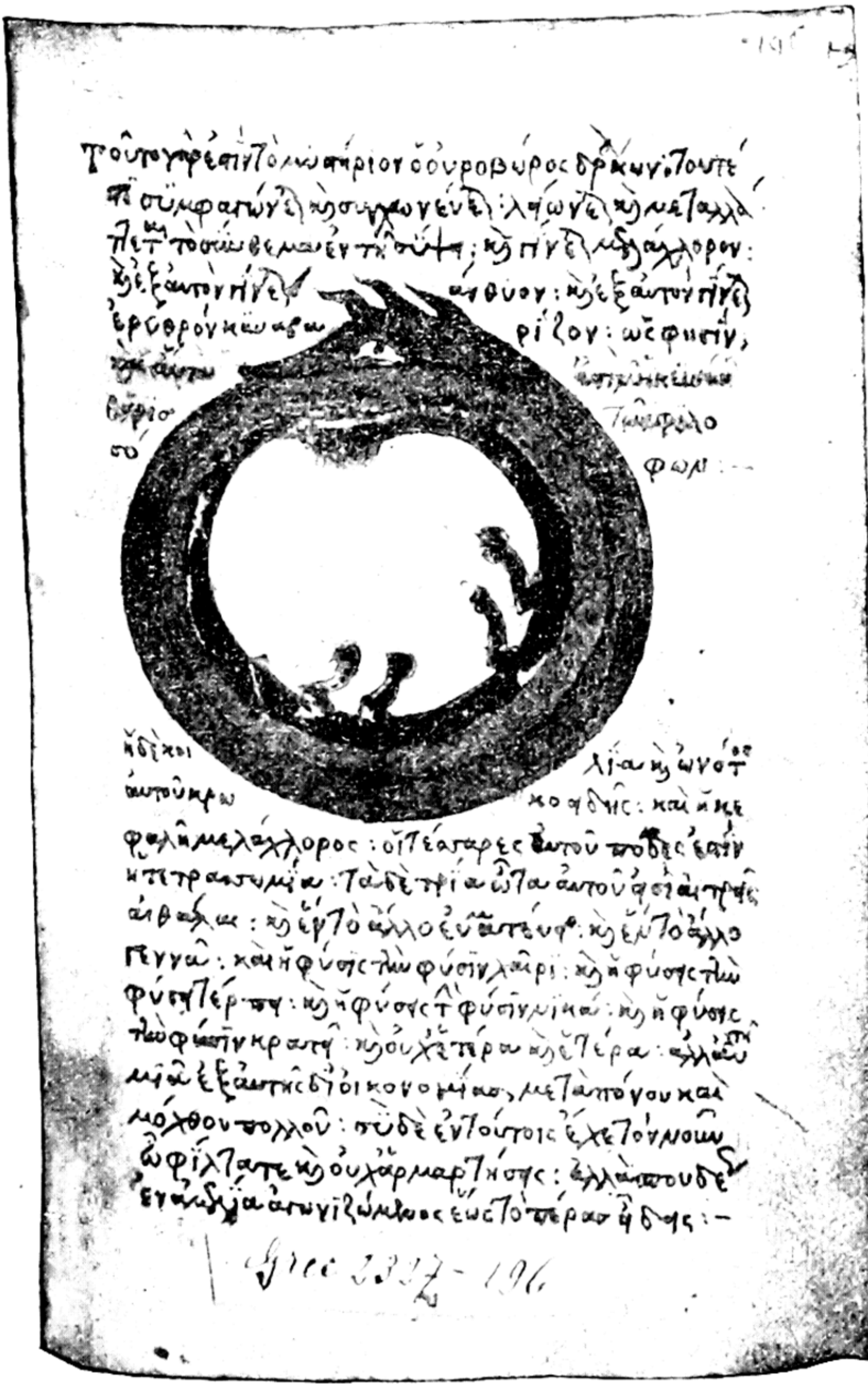
The atomic theory of Democritus (*c.* 400 B.C.) and the four-element theory of Aristotle (384–322 B.C.) were attempts to explain the nature of matter. They differed, however, from our modern theories by being based on a very small measure of fact coupled with a great deal of philosophical theory. The four-element theory

of Aristotle held the field for nearly 2,000 years. Its long continuance was due, probably, to the fact that it was vague enough to be stretched to explain, after a fashion, almost any phenomena and, while it could not be proved, it was extremely difficult to disprove. The theory held that all matter consisted of a sort of ' prime matter '

[*By kind permission of the Society for the Promotion of Hellenic Studies.*

FIG. 1.—These Drawings illustrate Types of Apparatus for Distillation and Sublimation used by the Greek Alchemists in the first Seven Centuries of the Christian Era and closely resembling that used in Chemical Work up to the close of the Eighteenth Century. (MS. Paris, gr. 2327, f. 81.)

which may be thought of as matter divested of all its properties. On this ' prime matter ' were superimposed the " elements," earth, water, air and fire, which we should to-day call the qualities of " earthiness, wateriness, airiness and fieriness." Earth represented the qualities of coldness and dryness ; water, coldness and wetness ;



[*By kind permission of the Society for the Promotion of Hellenic Studies.*

FIG. 1a.—The Serpent ' Ouroboros ' (the Tail-eater) was a Symbol denoting at once the Unity of Matter, and the ' Circulatory ' Type of Alchemical Process practised in certain Types of Alchemical Apparatus. (MS. Paris, gr. 2327, f. 196.)

air, hotness and wetness; fire, hotness and dryness. The varied qualities of the different kinds of matter were believed to result from differences in the proportions of the "elements" contained in them. No real system of chemistry was or could be built up on such a vague theory.

In the works of a number of authors who lived in Alexandria and other towns of Egypt during the first three centuries of the Christian era, we find the first sources of the traditions of chemistry and alchemy. These authors are the first to speak of the 'Sacred and Divine Art,' later called by them 'Chemia' or 'Chymeia,' a name transformed by the Arabs into the word we now use in the form of 'Alchemy.' This 'Sacred and Divine Art' was not, it is true, a science of chemistry, but rather a set of methods for 'making' gold, silver, purple [1] and precious stones. The works of these authors contain hundreds of recipes intended to produce gold or silver; some of them represent deliberate debasement and falsification of precious metals, others serious and systematic efforts to make them artificially. This tradition of metal working, the beginning of alchemy, was probably derived from the secret knowledge of the Egyptian priesthood, from which also may be derived the strange mixture of practical metallurgy with magical and superstitious beliefs which we always find in alchemy. These early alchemical authors were the first laboratory-workers and introduced us to almost all the simple pieces of chemical apparatus. The distillation apparatus is described by an author of the third century A.D., and the illustration (Fig. 1), taken from a Greek MS. copied in the Middle Ages, shows it to be very little different from that used to-day. The flask, basin, stillhead, receiver, pestle and mortar, crucible and furnace, water bath and sublimation apparatus were all brought into use in the first three centuries of the Christian era. Very little which is authentic is known about the inventors of these early types of chemical apparatus, but perhaps 'Mary the Jewess,' who lived in Egypt in the first century A.D., is to be regarded as the inventor of the distillation apparatus, of the water-bath (still called *Bain-marie* in France), and of the various types of sublimation apparatus.

These early authors who wrote voluminously on alchemy in Egypt and Byzantium in the first seven or eight centuries of the Christian era did not bring about much advance in our chemical knowledge. It appears likely that only one or two of the earliest authors, such as Mary the Jewess, Democritus [2] and Zosimus (third century) were practical alchemists with experience of the laboratory

[1] The dye derived from the murex shell-fish and greatly valued by the ancients.

[2] Not the Democritus of the Atomic theory, who died some 400 years earlier.

and its difficulties. The later Alexandrian and Byzantine authors were content to theorise about alchemy without practising it; moreover, even the most practical of these Greek alchemists were so much interested in making gold that they omitted to mention anything which did not seem to them to be relevant to the making of precious metals. Thus very few of the chemical discoveries they undoubtedly made have been recorded.

## 5. Chemistry under the Arabs

It is fairly certain that the Arabs, who rose to power in the seventh century A.D., first gained their knowledge of alchemy, directly or indirectly, from the Byzantine authors' works. The Arabs were, however, a more practical race than the Greeks, and alchemy under them made considerable strides. The discovery of sulphuric acid, nitric acid, *aqua regia*, silver nitrate, borax and corrosive sublimate are possibly, though not certainly, to be attributed to them; and though the Arabs were not the originators of their chemical methods and traditions, they undoubtedly used them in such a way as to increase the world's knowledge of chemical substances. They made little, if any, advance in our knowledge of the *nature* of chemical changes, but they prepared the way for real chemistry by the discovery of new substances, in particular the mineral acids, the lack of which had prevented any very extensive development in practical chemistry. The most important of the Arab alchemists was 'Geber'. The name of Geber is, however, attached to texts which were composed by several different authors. Thus the work containing the discovery of the mineral acids is known only in Latin and dates from the close of the thirteenth century: the majority of the Arabic works which bear the name of Geber (Jābir) date from near 1000 A.D. and we are doubtful whether any of these can be ascribed to the traditional Geber (Abu Musa Jābir ibn Hayyan) 702–766 A.D. Other notable Arab chemists were Iraqi,[1] Rhazes (*c.* 925) and Avicenna (980–1037).

The knowledge acquired by the Arabs was gradually handed on to the European peoples during the thirteenth and fourteenth centuries, and the alchemist, hardly known in Western Europe before this time, rapidly becomes an important figure. The work of the Arabs was carried on by such men as Albert Groot (Albertus Magnus)[2] 1193–1283 A.D., Roger Bacon (*c.* 1250) and Arnald de Villanova. Raymond Lully (b. 1224 A.D.) apparently brought about further notable advances. The discovery of the method of making

[1] A translation of one of his works by Dr. E. J. Holmyard has been published and is one of the few reliable translations of an Arabic alchemical work.

[2] Unique in being both a chemist and a Saint.

fairly pure alcohol, the action of acids upon metals, and the preparation of 'red and white precipitate'[1] are mentioned in his works, but there is some doubt whether these discoveries are not later work falsely attributed to him.

At this period, as indeed at all others, trickery was common enough, and a great number of fraudulent alchemists lived by their art, relying on a faked demonstration of gold-making to draw from

FIG. 2.—Manufacture of Acid for the Refining of Gold. (Agricola: *De Re Metallica*, 1553.) The apparatus is not very different from that in use twelve centuries earlier and 300 years later.

wealthy patrons money for further experiments which were never carried out or which proved unsuccessful. Alchemy fell thus into some disrepute, of which Chaucer's "Chanoune's Yeoman's Tale" is an amusing witness.

## 6. Chemistry in the Renaissance Period

In the early part of the sixteenth century there was great activity

[1] Mercuric oxide and amino-mercuric chloride.

in smelting and metallurgy, especially in the mining districts of Bohemia. This led to the industrial manufacture of acids (which were required for the separation of gold and silver), and also to the development of the assaying of ores, which was the foundation of chemical analysis. Agricola (Georg Bauer, 1494–1555) and Lazarus Erckern have left interesting accounts of the mining, metallurgy and technical chemistry of the time. This industrial chemistry was, of course, far more practical in character than alchemy.

A new direction was now given to chemistry by the work of Paracelsus. This man, whose real name was Philip Aureolus Theophrastus Bombast von Hohenheim, was a strange compound of genius and charlatan, and gave the world some ideas of genuine value wrapped up in a vast amount of verbiage and mysticism. His chief distinction was that he urged the value of mineral substances as medicines and directed the attention of chemists to other ends than the preparation of gold. He and his followers introduced the strangest mystical doctrines, believing all matter to be animated by spirits—sylphs,[1] pixies, gnomes and salamanders, who inhabited air, water, earth and fire respectively. Some of his followers were less grossly imbued with superstition, and Libavius and van Helmont, who lived in the latter part of the sixteenth century, come nearer to the type of the modern chemist. The former discovered the liquid stannic chloride and wrote a work *Alchymia*, which is clearer and more straightforward than any of those of his predecessors. Van Helmont, though somewhat superstitious and credulous, was a man of a true experimental spirit. He is perhaps most to be remembered for his invention of the word *gas*, and his study of certain gases, notably carbon dioxide. He recognised the existence of gases different from air, and realised that the gas found in old wells and caverns was identical with that formed by fermentation and by the action of acids upon calcareous rocks. The alchemist, Basil Valentine, who purported to have lived in the latter part of the fifteenth century, describes a great number of new facts. His best-known work *The Triumphal Chariot of Antimony* was, however, first published at the beginning of the seventeenth century and was probably written at that period by a salt-maker named Thölde. It mentions a great many facts about antimony and its compounds and describes a considerable number of other metallic compounds. Glauber (1604–1668) is best known to-day for his discovery of sodium sulphate—Glauber's salt—and its medicinal value.

During the period between the Greek alchemists (*c.* 300 A.D.) and Glauber (*c.* 1650 A.D.) chemical theory had made little or no progress. The Greeks held the four-element theory of Aristotle as

[1] The word *sylph* was invented by Paracelsus. Its derivation is unknown.

explaining the constitution of all chemical substances. The author of the Latin works ascribed to Geber (thirteenth century) thought of the metals as constituted of two elements, sulphur and mercury. These were not to be considered as the ordinary substances of those names but rather as the qualities of fieriness and colour (sulphur) and liquidity and metallic character (mercury). To these two elements Paracelsus added 'salt' as the quality of earthiness, astringency, etc. These theories, together with the four-element theory of Aristotle, held the field throughout the long period we have discussed and, indeed, were not extinct until the time of Lavoisier. They were too vague to be capable of disproof, nor indeed was any attempt at disproof compatible with the temper of the times. It was not until the sixteenth and seventeenth century that a spirit of scepticism arose which led men to question the grounds for the beliefs they held. The spirit of alchemy had always been akin to that of religion, a humble attitude to great men of the past who had once known the secrets of nature. A failure to understand the works of these men was attributed by the disciple to dullness on his own part, not to the ignorance, incorrectness or even muddle-headedness of the ancient authors he studied. Although most of the chemistry of Paracelsus was of a wild and superstitious character, we owe to him the very idea of a science of chemistry. Before his time there had been alchemy, metallurgy, pharmacy, but Paracelsus saw that in these and other activities there was the common factor of the transformation of one kind of matter into another. He declared that all these were a kind of alchemy, and so began to broaden that term from the pursuit of gold to the whole field of chemistry. None the less it was only after a hundred years in the early seventeenth century, that this idea began to bear fruit.

In the sixteenth and seventeenth centuries there arose a new spirit which manifested itself in the questioning of the foundations of belief. The geography of the ancients was disturbed by the discoveries of the western continents; Copernicus and Galileo upset the ancient notions of astronomy, and the questioning of the foundations of religion by would-be reformers uprooted the minds of the many from a slavish belief in the infallibility of the past. Aristotle's ideas about elements were often attacked in the sixteenth century, yet chemistry was one of the last of the departments of knowledge to be reconstituted as a science, and the reason for this tardiness was the fact that without a technique of measurement, which was not to be developed for many years, none of her fundamental laws could be discovered. Bacon and Boyle had to clear the ground of weeds before Priestley and Scheele could sow and Lavoisier and Dalton reap.

## 7. The Works of Francis Bacon

The founder of modern science must be considered to be Francis Bacon. In his *Novum Organum*, published in 1620, he laid down what he believed to be the true method of gaining knowledge. Francis Bacon, Baron Verulam, Viscount St. Albans (1561–1626) was from his youth struck by the inadequacy of the Aristotelian philosophy in its application to the sciences. He saw that man's knowledge of Nature was unsystematic and therefore ineffective. He considered that what we should to-day call science, should not be a mere knowledge of facts but should seek for the *imperium hominis*, that mastery of man over nature which the scientific worker of the last three centuries has gone so far to achieve. To his mind, the nature and first principle of things were not particularly important. He foreshadowed the point of view of the modern scientist who is not interested in the metaphysical question of what a thing *is*, but rather the practical question of what it *does*.

Bacon proposed a new way of investigating scientific problems. The first step was to be the collection of facts directly observed and freed as far as possible from personal prejudices and errors of observation. These facts were to be observed and surveyed without any attempt to fit them into a preconceived scheme or philosophy, and from the likenesses and differences of these facts, "notions" or conceptions of common properties and laws were to be formed.

This inductive method of collecting instances of a phenomenon is Bacon's great contribution to science. It is true, however, that the inductive method is rarely consciously used in science, but it lies at the root of all scientific thinking. The most valuable part of Bacon's work was not so much that he procured the use of this new method of investigation, but that he brought out the value of observation and the collection of facts, and pointed out the dangers of trying to fit observations into preconceived theories.

He struck a blow too at the Aristotelian philosophy, a blow which rendered it easier for Robert Boyle to lay down a sound foundation for modern chemistry.

## 8. The Foundation of Modern Chemistry

In the year 1660 occurred a great event, the foundation of the Royal Society, the purpose of which was the scientific study of nature. It provided a meeting-ground for all the scientifically minded and provided a means of discussing and publishing scientific works. One of its leading spirits was Robert Boyle (1627–1691).

His greatest contribution to chemistry was the declaration that the "elements" or first principles of which matter was composed

were not to be limited to three as by Paracelsus or to four as by Aristotle. Boyle revived the atomic hypothesis which had been held by Democritus and Lucretius and at intervals by other philosophers, and showed its value in explaining chemical changes. He was the first to give the word "element" its modern meaning of a substance not further to be analysed into simpler substances, and was the first to bring out the distinction between elements, compounds and mixtures. His work, *The Sceptical Chymist*, may be taken as the first document of modern chemistry. Boyle also distinguished himself in physics; his work on the relations between the pressure and volume of gases being particularly well known. The character of Boyle's writings, his clearness and freedom from the obscurity and superstition of the alchemists, did much to redeem the study of chemistry from the questionable character some of the mediæval alchemists had given it—an aroma such as clings round astrology and fortune-telling to-day.

In Boyle's own words we may say of the alchemists:—

"A person anything vers'd in the Writings of Chymists cannot but discern by their obscure, ambiguous, and almost Aenigmatical Way of expressing what they pretend to Teach, they have no mind to be understood at all, but by *the Sons of Art* (as they call them) nor to be understood even by these without Difficulty and Hazardous Tryalls. Insomuch that some of Them Scarce ever speak so candidly, as when they make use of that known Chymical Sentence: *Ubi palam locuti sumus, ibi nihil diximus.*" [1]

To the remarkable and apparently fabulous statements of alchemical authors and some of the stories retailed by the more credulous of his own time, Boyle was wont to say simply that:—

"He that hath seen it hath more Reason to beleeve it, than he that hath not."

a perfect statement of the scientific attitude to evidence.

Robert Boyle founded the science of chemistry and made of it the study of the nature and composition of matter instead of, as before, a mere means of preparing medicines or making gold.

Between 1660 and 1675 three English men of science, Robert Boyle, Robert Hooke and John Mayow, carried out what may be called the first extensive chemical researches. The air-pump was invented in 1654. Robert Hooke (1635–1703), who was a man of much experimental skill, devised an improved air-pump, and with this he and Boyle established the fact that combustion could not, in general, take place without the presence of air. Nitre seemed to act in the same way as air, for it was known that gunpowder would burn without access of air and Boyle showed it would burn

[1] Where we have spoken openly, we have said nothing of importance.

even in a vacuum. Hooke realised that when combustion took place, the combustible in some sense dissolved in the air (as a metal dissolves in an acid): he considered that air and nitre had a common constituent. John Mayow, in his work published in 1674, went still further. He showed clearly that in combustion only a part of the air was used up, this being the constituent common to nitre and air. These men, then, almost reached the true view of combustion, namely that the combustible combines with the oxygen in the air and leaves the nitrogen unaffected. If they had prepared pure oxygen their case would have been irresistible, but, as it was, their theories were displaced by one which was much farther from the truth—that of the fiery principle *phlogiston*.

On the Continent, Kunkel (1630–1702), whose share in the discovery of phosphorus is mentioned in Chapter XVIII. of this book, did something of the same work as Boyle, in helping to free Chemistry from the alchemical beliefs and superstitions.

Modern chemistry was now fairly launched, but before any clear view of chemical phenomena could be attained it was necessary that the nature of air, of water, and of combustion should be understood; and these studies were not brought to a satisfactory conclusion until the close of the eighteenth century.

## 9. The Phlogistonists

Stahl (1660–1734), who developed the Phlogiston theory of combustion, originated by Becher, was the most important chemist of the early eighteenth century. The theory, though erroneous, was not valueless, for it afforded a means, previously lacking, of classifying and explaining chemical facts. Stahl put forward a theory that a substance phlogiston (= fiery matter) was present in all combustible bodies and that combustion was *a release of phlogiston*. Thus Stahl believed that, when lead was heated, the consequent change to a yellow powder (litharge, lead oxide) was due to the loss of the phlogiston originally contained in the metallic lead. The subsequent change of the yellow litharge to 'red lead' he regarded as a further loss of phlogiston. The theory explained a certain number of facts, such as the preparation of metals by smelting. Thus if lead which had lost phlogiston (lead oxide) were heated with a substance such as carbon or wood, which was combustible and therefore contained much phlogiston, the phlogiston of the carbon returned to the 'dephlogisticated' lead (lead oxide), thus forming ordinary lead. If we substitute for 'phlogiston' the words 'absence of oxygen' the explanations of the phlogistonists become true. The theory is in fact a kind of negative method of expressing the

true facts about combustion. The theory broke down, however, as soon as any *quantitative* means of testing it were applied.

It is remarkable that in spite of the teaching of Bacon and of Boyle, few if any attempts were made to test the truth of the phlogiston theory by experiment. The theory had from the first obvious weaknesses. It did not explain the well-known fact that air was needed for combustion. Attempts were made to say that space was needed into which the phlogiston from the burning body might escape or that the air became ' saturated ' with phlogiston, but these explanations were hardly such as would satisfy a critical spirit.

The death-blows of the phlogiston theory were the discovery of oxygen and the general recognition of the fact that the products of combustion were *heavier* than the combustible body. Loss of phlogiston could only make the combustible substance lighter, unless the very improbable view were taken that phlogiston had a negative weight.

The eighteenth century saw a great increase in the number of chemical substances known. In Sweden, Carl Wilhelm Scheele (1742–1786), though he contributed nothing to chemical theory, discovered a great number of chemical substances, including chlorine, hydrofluoric acid, arsenic acid, lactic acid, oxalic acid, citric acid, tartaric acid and several other organic acids. He investigated the nature of manganese, barium hydroxide, hydrogen sulphide and arsine. This list of his discoveries is far from complete, and Scheele must be regarded as the pre-eminent discoverer in chemistry.

Joseph Priestley, in England (1733–1804), perfected the apparatus for handling gases which had previously been used by Stephen Hales (1677–1761), and by means of it carried out the first extensive study of gases. Priestley was no theorist, but rather a most capable investigator. He studied the different kinds of gases by the use of the pneumatic trough and other apparatus which he invented ; and in this way he discovered, or at least prepared in a pure state for the first time, the gases oxygen, nitric oxide, hydrogen chloride, sulphur dioxide, silicon fluoride, ammonia and nitrous oxide. His discovery of oxygen was perhaps his most important service to chemistry. Priestley was a phlogistonist to the last, but his discovery of oxygen became in the hands of Lavoisier the means of destroying the phlogiston theory.

During the last quarter of the eighteenth century quantitative chemical research had begun and some attempts were made to investigate the proportions in which chemical substances combined. The work carried on by Joseph Black (1728–1799) at Glasgow cleared up the relationship between carbon dioxide, chalk, lime, magnesia,

magnesium carbonate, caustic soda and sodium carbonate, by means of a *quantitative* study. These researches attracted great attention at the time and certainly helped to give the scientific world a clearer idea of the nature of chemical combination. At a slightly later period the remarkable and eccentric genius, Henry Cavendish, carried out his famous researches upon the composition of water. These are further described in Chapter IX.; suffice it to say here that he proved that water was composed of one volume of oxygen (dephlogisticated air) combined with two volumes of hydrogen (inflammable air). Cavendish, however, hardly appreciated the importance of his discovery from the point of view of the theory of combustion, and it remained for Antoine Laurent Lavoisier (1743–1794) to do away with the phlogiston theory and to propound a true theory of combustion.

## 10. La Révolution Chimique

It is, perhaps, not too much to say that chemistry after the work of Lavoisier and Dalton becomes *modern* chemistry and that in the chemical theories of the early nineteenth century, though there is much left unexplained, there are no serious fallacies or false beliefs such as might hinder the progress of the science. Lavoisier might have carried on his researches and made himself an even greater figure among the founders of modern chemistry, had not the French Revolution sent him to the guillotine. He had been one of the *Fermiers-généraux*, and against these the resentment of the revolutionaries, headed by Marat, was most strongly aroused. His attainments did not save him, for Coffinhal declared in words which none the less did an injustice to the spirit of the Revolution "*La République n'a pas besoin des savants.*" Lavoisier's researches are described in further detail in Chapter XIX. It may shortly be said that he grasped the significance of Priestley's discovery of oxygen, that he demonstrated conclusively that combustion was a combination of the combustible substance with oxygen, and he showed that the weights of the products of combustion were the exact sum of the weights of the combustible and of the oxygen taking part in the combustion. Phlogiston was thus rendered an unnecessary assumption.

Lavoisier and his followers thus initiated *La Révolution Chimique*. They got rid not only of the phlogiston theory but also of the terminology based on it (dephlogisticated air = oxygen, etc.) and invented the new names oxygen, hydrogen, etc. The acceptance of the new beliefs was slower in countries other than France, but by the year 1800 the phlogiston theory was almost everywhere extinct.

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It will be sufficient to summarise the subsequent progress of chemistry, for to discuss it in detail would be to recount facts which will be studied in the ensuing chapters of this book.

## PROGRESS OF CHEMISTRY DURING THE NINETEENTH CENTURY

### 11. The Structure of Matter

Progress in this direction was at first slow. The work of Dalton (Chapter II.) showed very clearly that matter behaved as if it had an atomic structure rather than a continuous one. The development of the kinetic theory by Clerk Maxwell and others supported the belief in the atomic character of matter. None the less it was not till the last decade of the nineteenth century that any reliable information as to the size and other properties of the atom was reached. The study of radio-activity and of spectra during the twentieth century threw much light on the structure of the atom (Chapter VII.), but it has only been during the last thirty years (1920–1952) that it has been possible to start the task of showing how the structure of the atom is related to the chemical properties of the elements.

The development of the idea of valency from about 1840 onward led to the study of the structure of the molecule and to extensive studies of the structural formulæ of compounds ; in particular of the compounds of carbon. It is only recently, however, that we have obtained any direct physical evidence of the way the atoms are distributed in the molecule and of their relative motions. This evidence, provided by the study of dipole moments, X-ray reflection and diffraction spectra, molecular spectra, etc., agrees very well with our theoretical deductions of structural formulæ. A considerable number of molecules have been studied ; but in no case have the results proved inconsistent with the older formulæ derived from chemical evidence. These newer studies make the knowledge we already possess more full and precise. Thus in the molecule of water, as we knew before, the two hydrogen atoms are both attached to the oxygen atom ; the newer physical methods give the additional information that the two H–O linkages are inclined at an angle of about 109°.

### 12. The Preparation of New Compounds

A knowledge of the existence of *types* of compound (such as acids, salts, etc.) had led even in earlier years to the possibility of predicting the existence of new compounds. It needed no great ingenuity to predict that a newly-discovered metal would have a

chloride or an oxide, and it is easy to devise ways of attempting to prepare such compounds as these. The greatest advances in the preparation of new compounds were due to the discovery of the fact that *groups of atoms*, such as $NH_4$— ammonium, $C_6H_5$— phenyl, CN— cyanogen, could react like single atoms, and it is to this discovery, due mainly to Liebig and Wöhler, and to the perfecting of structural formulæ, that the preparation of some 300,000 organic compounds is due.

## 13. Chemical Theory and Laws

The advances in this direction have led to the rather unfortunate elevation of the theory of chemistry into a special subject, "Physical Chemistry," so called because many of its departments involve study of methods and forces, etc., previously classified as 'Physical.' It is impossible to give any concise account of a century's progress in chemical theory. Suffice it to mention the discovery of the mathematical expression of the laws of electrolysis, and of the phenomena attending it; the ionic theory and the recognition of the peculiar character of solutions of acids, bases and salts; the investigation of the speed of chemical reactions and the study of chemical equilibria. These are a few of the major departments of chemical theory; innumerable minor points have been investigated and chronicled.

## 14. Present Progress

At the present date the progress of chemical discovery is as rapid as ever. Throughout its history discovery has never progressed steadily along the whole front of chemical knowledge. A new fact suddenly throws a light on an old unsolved problem and unravels its secret. The new knowledge so obtained opens up fresh avenues of discovery, and rapid progress takes place till further apparently insoluble problems are reached. In this way chemical knowledge increases irregularly and by 'spurts.' Of recent years (1920–1952) the chief advance is taking place in the direction of connecting our knowledge of atomic motions derived from spectra, etc., with the chemical and physical behaviour of the elements, and of gaining a knowledge of the real mechanism of chemical combination.

The study of crystal-structures is throwing much light on the structures of molecules which could not be investigated by the older chemical methods.

The last few years have also seen a remarkable advance in our methods of handling exceedingly minute quantities of material, and the discovery of several new elements has resulted from the application of delicate electrical methods to the separation and detection of minute proportions of these elements from great quantities of material.

Perhaps we may say that the chemical and physical worlds are now alike concentrating their attention on the individual molecule, the atom, the electron and their relationship and structure ; and it is perhaps, not too much to say that a second *Révolution Chimique* is taking place as a result of a fuller understanding of the atoms and molecules which for a hundred years we have represented in our chemical formulæ without any knowledge of their complex and remarkable structure.

## CHAPTER II

## CHEMICAL CHANGE

**15. Chemical and Physical Changes.**—Changes in a body may be of two types—chemical and physical. There is no sharp dividing line between the two, but it is in very few cases that we are in doubt under which heading to place a particular change. In general we may say that a **physical change affects only a few of the properties of a substance and gives us no reason to suppose that a new substance has been formed.**

**A chemical change, on the other hand, is accompanied by such a complete alteration of the properties of the substance that we are led to believe that a new substance has been formed.**

Thus, for example, if iron is magnetised, its density, colour, tenacity, specific heat and chemical properties remain unaltered. This is clearly a physical change.

When water is heated until it vaporises, the steam formed has all its physical properties entirely different from those of water. The fact that the chemical behaviour of steam is the same as that of water at the same temperature, and the fact that cooling reconverts steam into water, makes us believe that it is the same substance as water and that its vaporisation is a physical change.

If we heat a mixture of oxygen and hydrogen to 100° C., the density and one or two other properties alter, but not to the extent which would lead us to believe that any new substance is formed. On the other hand, if we heat the gases, contained in a stout vessel, by means of an electric spark, we find that a sudden and large rise of temperature and pressure occurs, together with a flash of light and the production of sound. Much energy is liberated. After the products have cooled, we find a small quantity of a liquid—water—which is obviously a new substance, differing in almost every particular from the oxygen and hydrogen from which it was made. A new substance has been formed, and the change is a chemical one.

**16. Distinctions between Chemical and Physical Changes.**—Three criteria serve in practice to distinguish chemical changes from physical changes.

(1) *Chemical changes are accompanied by an alteration in most of the properties of the reacting substances, while physical changes affect*

*but few of these properties.* This is nearly always true, but certain double salts and other loose compounds may strongly resemble the components from which they are formed. The fact of a profound change in the properties of two substances when mixed indicates the formation of a compound, and this affords us a means of distinguishing compounds from mixtures (§ 19).

(2) *Chemical changes are usually permanent in character, while physical changes as a rule persist only so long as the exciting cause remains.*

Thus the water formed from oxygen and hydrogen by the action of heat will not revert on cooling to these elements, while steam produced by heating water will form water once more on cooling. There are a number of reversible chemical reactions to which this criterion does not apply, but these are usually distinguishable from physical changes on other grounds.

(3) *Chemical changes produce, as a rule, more energy than do physical changes.* Thus the formation of a gram of water from oxygen and hydrogen produces 3,833 calories, while the melting of a gram of ice produces 80 calories, and the condensation of a gram of steam 536 calories. There are, however, many chemical changes which are accompanied by very small energy changes. In practice, however, a marked change of temperature indicates the formation of new compounds, and, therefore, a chemical change, while a change accompanied by the production or absorption of but little energy may be chemical or physical, but is more likely to be the latter.

**17. Substances.**—Chemistry is concerned with the description and recognition of 'substances,' and it is necessary to understand what is meant by a 'substance' in the chemical sense.

We should not call a motor car or a parrot 'a single substance,' for both of these objects contain recognisably different kinds of material. We might, on the other hand, call milk or copper or glass 'substances,' because *they appear to consist of a single kind of material with properties* (i.e., *qualities*), *sufficiently constant and well marked to distinguish them from other kinds of material.* For thousands of years the notion of the existence of substances has been extant, but the idea of 'pure substances' was not grasped before the time of Robert Boyle. Pliny (*c.* 50 A.D.) mentions about a dozen kinds of the material which we call 'common salt,' some white, some yellowish, some in lumps, some in powder, etc., and apparently it did not occur to him that all these kinds of salt consisted of one single substance, 'pure salt,' mixed with impurities of different kinds. He thought of them, rather, as separate species, differing from each other, as, for example, a donkey differs from a horse.

The idea of pure substances was to some extent realised by

Boyle, but it was not till the early eighteenth century that the idea that a particular element or compound is distinguished from all others by specific, invariable and characteristic properties was arrived at; and this notion was necessary for a true grasp of the idea of the chemical compound. Boyle, however, gave a real and definite meaning to the term *element*, which is perhaps the primary chemical conception.

**18. Elements.**—Even before the idea of 'pure substances' was developed, it was recognised that one kind of matter could be transformed into another, and the conclusion was reached that all known substances were combinations of a few *elements* which themselves were simple, *i.e.*, not composed of any other kind of matter. The early theories about these elements are described in Chapter I. The first real step towards a knowledge of the nature of these elements was taken in the seventeenth century, when the principle was laid down by Boyle that every substance which had not been proved to be composed of two or more different kinds of matter should be regarded as an element.

The fundamental means of deciding whether a particular substance is an element is to find out by practical experimental tests whether it conforms to the definition of an element. This definition, based on the ideas of Robert Boyle, may be set out in the following form:

**An Element is a distinct species of matter which has not yet been shown to be composed of two or more different kinds of matter.**[1]

It follows, then, that in order to find out whether a particular substance is an element, we must attempt in every possible way to separate from it two different kinds of matter. The action of heat, of the electric current, and of other chemical elements or compounds are the methods employed to bring about such a separation.

To take an actual example, the substance copper is a distinct species of matter, that is to say, it is distinguished from other substances by having a specific colour, tenacity, melting point, density, etc., and by its behaviour when treated with other substances (chlorine, acids, etc.).

If we subject copper to great heat (in absence of air) it is not changed in any fundamental way. It melts, and finally boils, but does not separate into two definitely different substances. The

[1] It may be objected to this definition that chemical elements (*a*) can readily be split up into ions and electrons by an electric discharge; (*b*) may be transformed into other elements by bombardment with *a*-particles, protons, or neutrons. The following definition is more satisfactory:—

*A chemical element is a distinct species of matter which cannot be converted by the action of heat, chemical reaction with other substances, or small electrical potentials into two or more electrically neutral different kinds of matter.*

action of electricity has no effect on the solid or liquid. Electricity may ionise the vapour, but does not separate it into two or more different elements. If we treat copper with other elements, such as oxygen or chlorine, the product is a single substance not two different ones. We conclude, therefore, that copper is an element, for our attempts to split it up are unavailing.

If, on the other hand, the metal brass were subjected to the same treatment, we should find that, when strongly heated in a vacuum, it underwent a change. The metal at a white heat would be found to evolve a vapour which would condense on a cold surface as a white metal, and a red metal, copper; would be left behind. The brass would thus be separated into two different substances, and could not be called an element. Alternatively, the brass might be heated in a current of chlorine gas, itself an element. The products might be dissolved in water and electrolysed (§ 112) using a small voltage.[1] A red metal—copper—would be deposited on one electrode. We should then have separated from the brass a substance different from itself, and so we should not regard it as an element.

A characteristic of pure substances is that they possess a fixed composition under a variety of conditions, in particular they will cross a phase boundary (§ 87), that is pass from the solid to the liquid, or from the liquid to the vapour, without a change in composition under various conditions. Mixtures are commonly separated by distillation or crystallisation, thus illustrating the change in composition of ' impure substances ' on crossing a phase boundary.[2]

**19. Mixtures and Compounds.—A ' pure substance ' may be said to be a single species of matter distinguished by displaying, under given conditions, characteristic and invariable properties.**

Thus we call water a pure substance, because at 4° C. 1 c.c. always weighs 1·0000 gm.; because, under normal atmospheric pressure, it always freezes at 0° C.; because it always evolves heat when added to sulphuric acid, etc. It is not any *one* of these properties which makes us call water a pure substance, but the fact that a considerable number of these accurately definable properties are always associated with any water from which appropriate steps have been taken to remove foreign substances.

We may summarise the relations between elements, compounds, and mixtures as follows :—

[1] So as to deposit the copper and not the zinc.

[2] Some mixtures do cross a phase boundary, at a certain temperature and pressure without change of composition. The constant-boiling mixture of 20·22 per cent. HCl, 79·78 per cent. $H^2O$, boiling at 108·5° C. under a pressure of 760 mm. is one such. But if the pressure be changed then the composition of the vapour phase changes, and some separation of the constituents of the mixture is achieved, whereas a pure substance will boil without a change in composition under a variety of pressures.

**Every portion of matter consists either of a single pure substance or a mixture of two or more pure substances, each of which is either an element or a chemical compound.**

We have seen how elements and pure substances can be distinguished from any other kind of matter. It is now necessary to find experimental tests by which we can distinguish a *chemical compound* from a *mixture* of elements or chemical compounds by a series of experimental tests.

**20. Homogeneity of Compounds.**—A *homogeneous* substance is one of which any portion taken at random has the same composition and properties as every other portion. A *heterogeneous* substance is one which does not conform to these conditions.

It will easily be seen that a chemical compound, which contains only one kind of matter, must be homogeneous, while a mixture need not necessarily be so. It may be possible to perceive the different constituents of a heterogeneous mixture by inspection with the naked eye or microscope. It is not always, of course, possible to see the constituents of a mixture, for they may be indistinguishable in appearance, or, again, the particles may be too small to be seen. Thus red ink, though it is certainly a mixture of a red dye and colourless water, shows no sign of separate red particles floating in clear water however much it is magnified. India ink, on the other hand, when magnified 1,000 times, shows tiny particles of carbon suspended in clear water.

Thus a compound *must* be homogeneous, for it contains only one kind of substance, while a mixture may or may not be homogeneous.

*A heterogeneous substance must be a mixture if it remains heterogeneous over a range of temperatures and pressures.*

A pure substance can exist as an heterogeneous system, one phase of the compound suspended in another, but only at a unique temperature and pressure. For example, ice crystals suspended in water, in contact with water vapour, can exist at 0·0075° C. under a pressure of 4·58 mms. (the so-called triple point), but under no other conditions, whereas a mixture can remain heterogeneous over a whole range of temperatures and pressures.

**21. Separation of the Constituents of Compounds and of Mixtures.** The constituents of most compounds are held together by considerable forces, while those of most mixtures are held together by small or negligible forces. It therefore often requires much energy to separate the constituents of a compound, and very little, or none, to separate those of a mixture.

Thus to separate 18 gms. water into its constituents, oxygen and hydrogen, a large amount of energy (equivalent to 69,000 calories) must be spent, while in order to separate oxygen and hydrogen from a gaseous mixture of the two little or no energy is required, mere

diffusion through a porous tube (§ 54) being enough to effect a separation.

In general, then, if it is possible to separate the constituents of a substance by means which involve the expenditure of very little energy, the substance is probably a mixture. Such methods as flotation (§ 405), hand-picking, magnetic separation (§ 1011), washing (§ 324), diffusion (§ 598), fractional crystallisation (§ 86), freezing out a less volatile or less fusible constituent (§ 720), evaporation at room temperature, etc., may serve to split up mixtures but not compounds. References are given to examples of such separations described in the later part of the book.

Compounds are usually split up only by such means as strong heat, the action of electricity or the chemical action of other substances.

A more definite distinction may be made by saying that mixtures (1) can be split up by comparatively feeble forces acting on their particles, *e.g.* friction (washing and winnowing), magnetic forces (magnetic separation), or (2) may split up spontaneously through differences in the velocity of their particles (diffusion, evaporation). Compounds, on the other hand, are split up only by fairly intense forces applied to their smallest particles: these may be chemical energy (collision of and electrical attraction between particles), heat energy (vigorous collision of particles), radiation (absorption of relatively large amounts of energy by individual particles), and electrical forces acting on particles with relatively intense electrical charges (ions).

**22. Constant Composition of Compounds.**—A chemical compound is distinguished from a mixture by having a *constant composition.* Thus pure calcium carbonate (chalk) contains exactly 11·993 per cent. of the element carbon, and never contains any more or any less. India ink, a mixture of water and carbon, may contain any proportion of the latter, and no one proportion of carbon can be fixed on as being characteristic of india ink. Again, a mixture of oxygen and hydrogen may contain any proportions of these gases, but the compound of oxygen and hydrogen, known as water, contains exactly 2·016 parts by weight of hydrogen to every 16 parts by weight of oxygen, and never any more or less.

**23. Boiling Points and Melting Points of Compounds and Mixtures.**—A compound, being a pure substance, has its own characteristic properties, and under fixed conditions of pressure has a definite melting point and boiling point. Thus, when a pure compound is heated, it does not begin to melt till a certain temperature is reached, and the compound remains at this temperature until it is entirely melted. In the same way a compound begins to boil at

a fixed temperature, and the boiling point does not change, however much of the liquid is boiled away.

Mixtures, however, rarely melt or boil at fixed temperatures. As a rule, melting or boiling begins near the melting point or boiling point of the more fusible or volatile component, and gradually rises until a point is reached near that of the melting or boiling point of the other component.[1] Thus a sharp melting point and a fixed boiling point are characteristic of a compound.

**24. The Formation of a Compound involves a Chemical Change.**—When a mixture is formed or broken up, there is only a *physical change*, while the formation or decomposition of a compound is accompanied by a *chemical change*, and therefore, as a rule, by the production or absorption of energy in the form of heat, light, etc., and by a complete change of properties (§ 16).

**25. The Structure of Elements and Compounds.**—Although the reader has not yet examined any of the evidence for the atomic structure of matter, and the electrical nature of the atom, it may be well to try to form a picture of the phenomena which underlie physical and chemical change, and which explain the existence of the classes of compounds known as elements, compounds and mixtures. The evidence for the assumptions which follow is largely derived from physics, and it is therefore not unreasonable for the student of chemistry to take them for granted at first. Chapter VII. goes into the matter more fully.

Matter is regarded to-day as entirely composed of atoms. These are exceedingly minute and exceedingly numerous. *Only one kind of atom is contained in each element;* it is therefore impossible to divide it up into simpler substances without splitting up the atoms of which it is composed. The atom itself is composed of from two to 330 particles (electrons, protons and neutrons), and its character as the atom of a particular element depends on the number of protons in its nucleus, the innermost portion of the atom. The nucleus is so small, and is bound together so firmly, that only enormous concentrations of energy can decompose it, and in chemical operations we find that atoms are neither created nor destroyed nor transformed into other atoms. It is not difficult to remove an electron or two from the outer portions of the atom, and this process (known as ionisation) may be regarded in some sense as a splitting of the atom. The removal of an electron or two does not, however, convert the atom into a different atom, for the nucleus remains unaltered and the atom will regain its lost electrons as soon as it meets with a suitable supply of them.

[1] See Chapter IV. Cryohydrates and constant boiling mixtures (p. 702) are exceptions.



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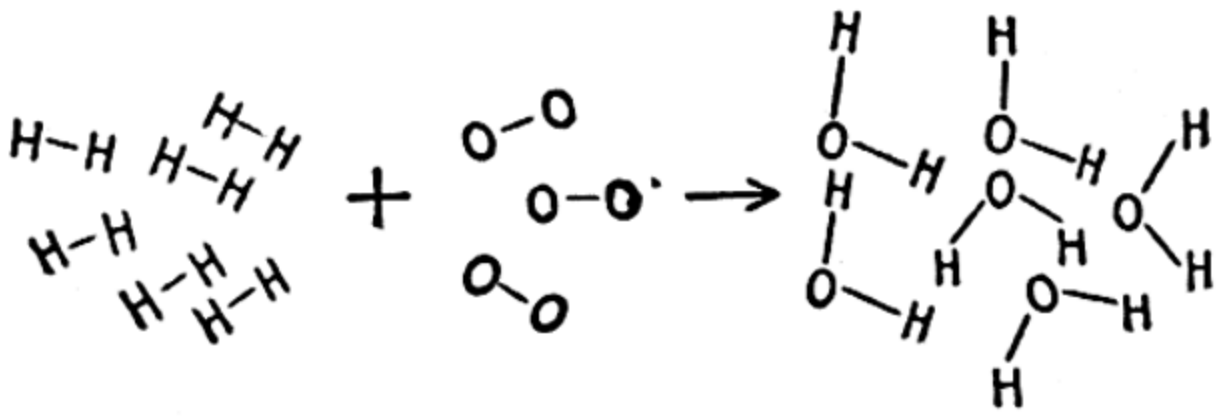
An element, then, contains only one kind of atom.[1] A compound is made up of molecules, which are particles all exactly alike and each containing a fixed number of atoms of two or more different kinds. The atoms in each molecule are bound together by electrical attraction, or by sharing one or more electrons. The forces binding these atoms together may be strong or weak. They never approach the strength of the forces which bind the inner electrons of the atom in their positions, and consequently moderate forces will serve to decompose compounds. In some cases the energy of the linkage between the parts of a molecule is very feeble, and it may break merely as a result of the forces set up by motion of the molecules in question. But, though the energy may be feeble, the minute size of the atoms in the molecule, and the extremely short distance between them, make the forces holding them together quite powerful: so much so that it is quite impossible to separate the atoms by mechanical means, such as flotation, diffusion, filtration, etc.

A mixture we conceive as containing two or more different kinds of atoms or molecules *not* held together by the sharing of electrons or any powerful electrical attractions.[2] Thus but small forces are needed to separate them, though the practical difficulty of applying the forces may be great. If the mixture is very intimate, as in the case of a solution, mechanical means of separation will be difficult to apply, though such processes as diffusion may be successful. If the mixture is coarser, each particle consisting of aggregates of thousands or millions of molecules, the separation is correspondingly easier.



| Molecules of hydrogen each consisting of two *atoms* of hydrogen. | Molecules of oxygen each consisting of two atoms of oxygen. | Molecules of water each consisting of two atoms of hydrogen and one atom of oxygen. |
|---|---|---|

Physical change is conceived as being an alteration in the motions, internal or external, of the atom or molecule, while a chemical change consists of *the formation of new molecules by an alteration in the number, kind, or arrangement of the atoms in other molecules*. Thus, when iron is made red hot, the vibrations of its atoms become ampler, and the electrons which they contain take up new positions,

[1] But see § 148.

[2] The particles of mixtures are often held together comparatively firmly by surface forces.

but no new molecules are formed. When a mixture of hydrogen and oxygen is exploded, new molecules are formed, and a new compound, water, with a new set of properties, appears.

There are some cases of changes which cannot be classified as chemical or physical; these occur when molecules or ions are associated by strong attractions without actually forming recognisable compounds. Examples are the absorption of ions by, e.g., clays, of hydrogen by palladium or of gases on a tungsten filament.

**26. Types of Chemical Changes.**—Several different types of chemical changes are distinguished. The reader unfamiliar with the use of formulæ should refer to §§ 37, 38.

(1) *Combination.*—When two or more substances unite to form a single product they are said to combine. Thus chlorine and sodium *combine* to form sodium chloride.

$$2Na + Cl_2 = 2NaCl.$$

(2) *Decomposition.*—When a single substance breaks up into two or more simpler substances it is said to decompose. Thus mercuric oxide when heated *decomposes* into mercury and oxygen,

$$2HgO = 2Hg + O_2,$$

and ferrous sulphate when heated *decomposes* into ferric oxide, sulphur dioxide and sulphur trioxide.

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

(3) *Dissociation* is a reversible decomposition of a compound. Thus ammonium chloride *dissociates* when heated into ammonia gas and hydrogen chloride, which on cooling again recombine, forming ammonium chloride.

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

(4) *Displacement.*—When an element reacts with a compound in such a way as to remove one element and itself combine with the remainder, it is said to displace the element. Thus zinc *displaces* copper from copper sulphate, forming zinc sulphate and metallic copper.

$$Zn + CuSO_4 = ZnSO_4 + Cu.$$

(5) *Double Decomposition.*—When two compounds (usually acids, bases or salts) react in such a way as to exchange radicals[1] they are said to undergo double decomposition. Thus lead nitrate and sodium sulphate give sodium nitrate and lead sulphate.

$$Pb(NO_3)_2 + Na_2SO_4 = 2NaNO_3 + PbSO_4.$$

Hydrochloric acid and silver nitrate give silver chloride and nitric acid.

$$HCl + AgNO_3 = AgCl + HNO_3.$$

(6) *Substitution.*—When an element or compound displaces another element from a compound and, at the same time, combines with the element displaced, it is said to be substituted in the compound. Thus methane and chlorine give methyl chloride and hydrogen chloride.

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

[1] Radical. A group of atoms which, in its chemical reactions, reacts as a unit analogous to a single atom.

The nitro-group $NO_2$ is *substituted* in benzene by the action of nitric acid upon it

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O,$$

or

$$C_6H_5.H + HO.NO_2 = C_6H_5.NO_2 + H_2O.$$

(7) *Hydrolysis.*—When a compound reacts with water in such a way that it splits up and forms two compounds, one with the hydrogen of the water, the other with the hydroxyl, thus

$$AB + H.OH = AH + BOH,$$

the compound is said to be hydrolysed. Thus thionyl chloride is hydrolysed by water forming sulphurous acid and hydrochloric acid.

$$O = S\begin{matrix}Cl\\Cl\end{matrix} + \begin{matrix}H.OH\\H.OH\end{matrix} = O = S\begin{matrix}OH\\OH\end{matrix} + 2HCl.$$

Methyl acetate is hydrolysed,

$$CH_3O.CO.CH_3 + HOH = CH_3OH + CH_3COOH,$$

forming methyl alcohol and acetic acid.

Hydrolysis is really a special case of double decomposition, but is such a common phenomenon that it is given a special name.

(8) *Addition.*—When a compound combines as a whole with another element or compound, forming a third compound, it is said to be added on or to form an addition product. Thus ethylene and bromine undergo an *addition* reaction,

$$C_2H_4 + Br_2 = C_2H_4Br_2,$$

and ferrous sulphate and nitric oxide do the same,

$$FeSO_4 + NO = FeSO_4 . NO.$$

Addition is actually a special case of combination, compounds rather than elements being concerned.

(9) *Isomeric and Tautomeric Change.*—When a compound changes into another compound without losing or gaining any matter it is said to undergo an isomeric change or internal rearrangement.

Thus ammonium cyanate changes into urea,

$$NH_4OCN = CO(NH_2)_2.$$

If such a change is reversible it is said to be *tautomeric.*

## ENERGY OF CHEMICAL CHANGE

**27. Chemical Energy.**—When chemical change takes place energy is liberated or absorbed, usually as heat, but occasionally as light, electricity or work. It is usually possible, however, so to arrange the conditions of the experiment that all the energy shall be liberated or absorbed in the form of heat.

A reaction which liberates heat energy is said to be *exothermic*, and one which absorbs heat energy is said to be *endothermic.*

When a reaction takes place the reacting substances have a certain total internal energy or *intrinsic energy* Q, and the products of the reaction have a different intrinsic energy Q′. Thus Q – Q′ represents the energy change of the system. This *difference* of energy Q – Q′ can be determined practically, but the actual intrinsic energies are not known.

**28. Hess' Law.**—It is found that a certain definite energy change is associated with each particular chemical change. The way in which the change takes place makes no difference ; *the heat evolved or absorbed in a chemical change depends only on the initial and final stages of the system, and is independent of the intermediate stages through which it passes.*

This generalisation is known as Hess' Law and follows from the principle of the conservation of energy. Suppose that when a given quantity of a substance A changes into a substance B by a certain set of reactions Q calories are evolved, and that when it changes by another set of reactions Q′ calories are evolved. Now transform A to B by the first method and B back to A by the second. Then Q − Q′ calories are produced, and by doing this an infinite number of times an infinite quantity of energy could be developed from an isolated system, contrary to the assertion of the law of conservation of energy.

Thus, to quote an example given by Mellor, let us suppose that, starting with a solution of 36·46 gms. hydrochloric acid, and 56 gms. of solid quicklime, we wish to make a solution of calcium chloride. We may do this in two ways.

(1) We may slake the quicklime with water, thus evolving 15 Calories, and dissolve this in water, 3 Calories being evolved in the process. We may then add the acid when a further 28 Calories are produced—a total of $15 + 3 + 28 = 46$ Calories.

Using the notation explained in § 29 :—

$$\left\{\begin{array}{r} CaO + H_2O = Ca(OH)_2 + 15 \text{ Cals.} \\ Ca(OH)_2 + Aq = Ca(OH)_2 \,.\, Aq + 3 \text{ Cals.} \\ Ca(OH)_2 \,.\, Aq + 2HCl \,.\, Aq = CaCl_2 \,.\, Aq + 2H_2O + 28 \text{ Cals.} \end{array}\right.$$

$$\overline{CaO + 2HCl \,.\, Aq = CaCl_2 \,.\, Aq + H_2O + 46 \text{ Cals.}}$$

(2) We may add the 56 gms. of quicklime directly to the solution of acid. If we do this, we find that 46 Calories are again evolved :—

$$CaO + 2HCl \,.\, Aq = CaCl_2 \,.\, Aq + H_2O + 46 \text{ Cals.}$$

A second example may be taken.

Thus, if we combine 64 gms. sulphur with 12 gms. of carbon and burn the carbon disulphide formed, we use up 19·6 Cals. in making the carbon disulphide, and liberate, when it is burned, 253 Cals., representing a total liberation of heat of 233·4 Cals.

$$\begin{array}{r} C + 2S = CS_2 - 19{\cdot}6 \text{ Cals.} \\ CS_2 + 3O_2 = CO_2 + 2SO_2 + 253 \text{ Cals.} \end{array}$$

$$\overline{C + 2S + 3O_2 = CO_2 + 2SO_2 + 233{\cdot}4 \text{ Cals.}}$$

or

If we burn the 64 gms. of sulphur and 12 gms. of carbon separately, we liberate 94·5 Cals. by burning the carbon, and 138·9 Cals. by burning the sulphur, again a total of 233·4 Cals.

$$2S + 2O_2 = 2SO_2 + 138{\cdot}9 \text{ Cals.}$$
$$C + O_2 = CO_2 + 94{\cdot}5 \text{ Cals.}$$
$$\overline{C + 2S + 3O_2 = CO_2 + 2SO_2 + 233{\cdot}4 \text{ Cals.}}$$

Thus the same quantity of heat, 233·4 Cals., is evolved by whatever means we convert our 12 gms. of carbon and 64 gms. of sulphur, and 96 gms. of oxygen, into 44 gms. of carbon dioxide and 128 gms. of sulphur dioxide.

**29. Heat of Reaction.**—The *heat of reaction* of a chemical change is the quantity of heat produced when the weights of the reacting substances indicated by the equation (§ 74) for the change react, the unit of mass being the gram. The heat evolved or absorbed is usually expressed as kilogram-Calories, abbreviated as Cals. The kilogram-Calorie (Cal.) is 1,000 gram-calories (cals.), and is the heat required to raise the temperature of a kilogram of water by 1° C.[1]

The heat effect is usually expressed in the equation. Thus the equation,

$$2Mg + O_2 = 2MgO + 291{\cdot}6 \text{ Cals.},$$

indicates that 48 gms. of magnesium burn in oxygen, producing enough heat to raise 291·6 kilograms of water through 1° C.

The determination of heats of reactions which take place in solution may readily be performed by ordinary calorimetric methods.

Thus, if we require the heat of reaction of hydrochloric acid and caustic soda in dilute solution, we may proceed as follows: Equal volumes of, say, tenth-normal solutions, which have been brought to the same temperature, are mixed in a calorimeter, of which the water equivalent is known, and the small rise of temperature is observed by a delicate thermometer. If the rise of temperature is $t$° C., the volume of each solution $n$ c.c. and the water equivalent of the calorimeter, thermometer, etc., is $w$, the heat produced by the reaction is $(w + 2n)t$ cals.[2] Ten litres of each solution contain 1-gm. molecule of the substances, and the heat produced by these quantities of the solutions would be

$$\frac{(w + 2n)t \times 20{,}000}{2n} = \frac{10(w + 2n)t}{n} \text{ Cals.},$$

which quantity represents the heat of reaction.

If the water equivalent is neglected, the heat of reaction will be $20t$ Cals

Where great heat is produced, and where gaseous products are formed special methods must be used. The bomb calorimeter is particularly useful for determining *heats of combustion*, that is to say, the heat produced when *1 gm. molecule of a combustible substance combines with oxygen*.

The bomb calorimeter is a steel vessel ($v$) lined with platinum or enamel.

[1] Usually from 0° C. to 1° C., but other ranges such as 14° C. to 15° C., etc., are used.

[2] The specific heat and density of these dilute solutions may be regarded as unity without appreciable error.

A weighed amount of the substance to be burned is placed in a capsule (*c*), in contact with a wire (*w*), which can be electrically heated. The bomb is then filled with oxygen at, say, 20 atmospheres pressure and is placed in a large vessel of water. When thermal equilibrium has been reached the substance is fired by means of a current passed through the wire. The temperature of the water is recorded and the rise noted. The number of Calories evolved by the combustion of 1-gm. molecule of the substance is calculated.

It is possible to find the *heat of formation* of a compound even when the elements concerned do not react directly. The procedure

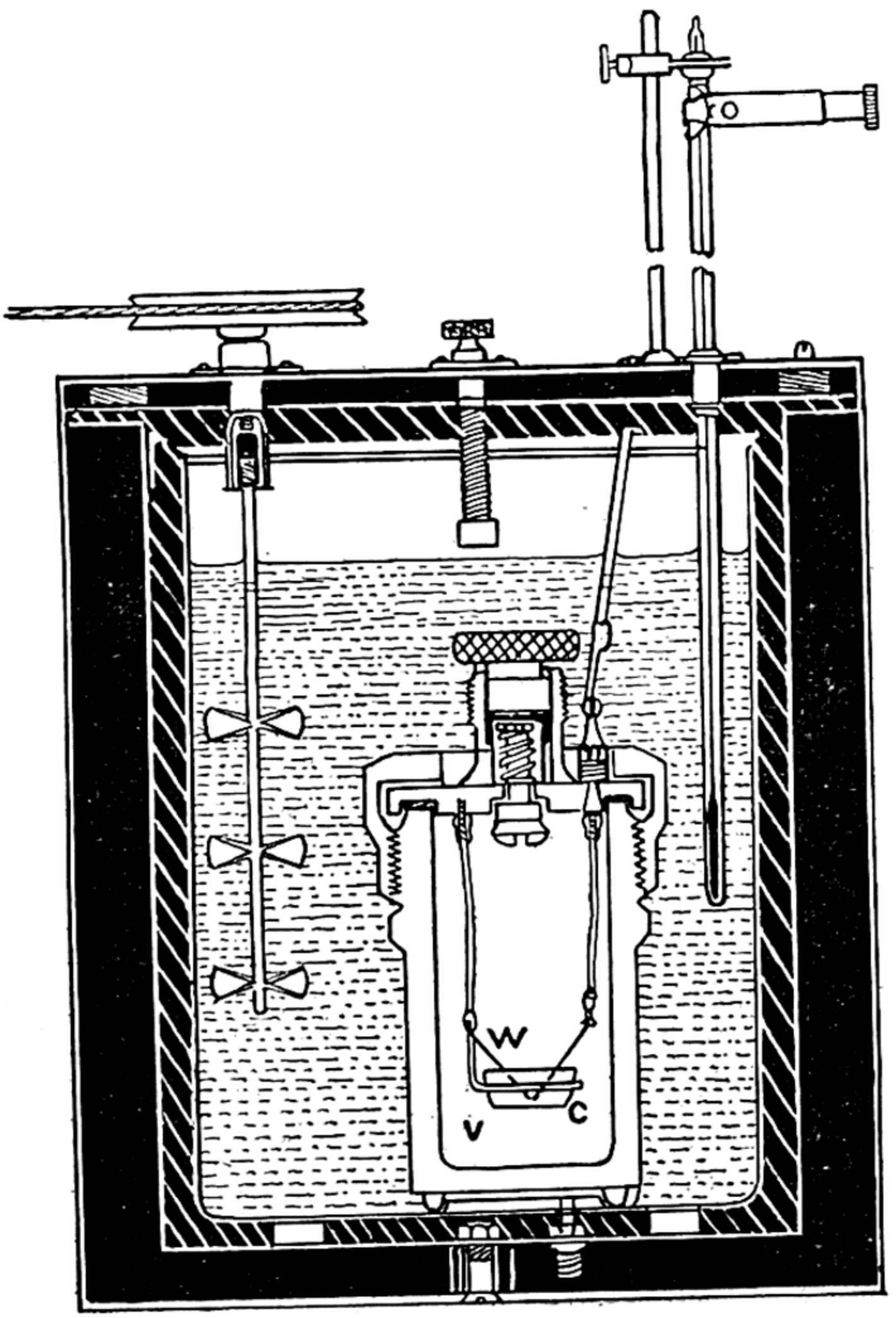



FIG. 3.—Bomb Calorimeter.

is best illustrated by an example. Thus the heat of formation of acetylene cannot be measured directly, for carbon reacts directly with hydrogen only under conditions which make it impossible to measure the heat produced. Now carbon and hydrogen combine and form acetylene, and acetylene burns in oxygen, forming carbon

dioxide and water. The *total* heat produced by these *two* processes

$$4C + 2H_2 = 2C_2H_2$$
$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$$

should be the same as that produced when the amounts of carbon and hydrogen indicated in the equation are burned directly to carbon dioxide and water without being converted into acetylene. We should therefore find that the equations :—

$$4C + 2H_2 = 2C_2H_2 + x \text{ Cals.}$$
$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O + 625{\cdot}8 \text{ Cals.}$$

which add up to—

$$4C + 2H_2 + 5O_2 = 4CO_2 + 2H_2O + (x + 625{\cdot}8) \text{ Cals.}$$

should give the same total heat as the two reactions following (the heats of which are readily measured)—

$$4C + 4O_2 = 4CO_2 + 377 \text{ Cals.}$$
$$2H_2 + O_2 = 2H_2O + 137 \text{ Cals.}$$

---

$$4C + 2H_2 + 5O_2 = 4CO_2 + 2H_2O + 514 \text{ Cals.}$$

It follows then that $x + 625{\cdot}8 = 514$, and that $x$, the heat of formation of 2-gm. molecules of acetylene is $-$ 111·8 Cals., and the heat of formation of acetylene is then $-$ 55·9 Cals.

## MASSES INVOLVED IN CHEMICAL CHANGES

**30. Conservation of Mass.**—Long before the energy changes associated with chemical combination had been studied, much attention had been given to the relation between the weights of reacting substances. These studies led to the establishment of a series of fundamental chemical laws which enabled Dalton to enunciate his Atomic Theory on which the whole of modern chemistry is based.

The Law of Conservation of Mass states that **the mass of a system is unaltered by any change which takes place within it,** or, expressing the law in a form more directly applicable to chemistry, **the total mass of the substances taking part in a chemical change remains unaltered throughout the change.**

This law was first stated by Lavoisier, and no evidence of any measurable departure from it has been produced. Very exact experiments were performed by Landolt, who sealed up substances capable of chemical reaction in the separate portions of a vessel of the type shown in Fig. 4. This vessel contained a cup which could contain one reagent, the other being placed in the space outside it. An evacuated jacket, like that of a thermos flask, eliminated the disturbing effects of the heat of reaction on the volume and the consequent apparent weight of the vessel. The vessel was

weighed with elaborate precautions to ensure accuracy, and then inverted, causing the substances to mix and reaction to take place. The vessel was then again weighed. No change of mass greater than the very small experimental error (about 1 part in ten million) could be detected. It must be remembered that this law, like all others, is only a statement of ascertained facts, and not a self-evident truth. The Law of Conservation of Mass is the fundamental basis of every chemical analysis or determination, and, although millions of these have been performed, no errors have been found which could be attributed to a failure of the Law of Conservation of Mass. We may therefore assume with almost complete certainty that no change of mass of an amount measurable by our present instruments occurs during a chemical transformation.

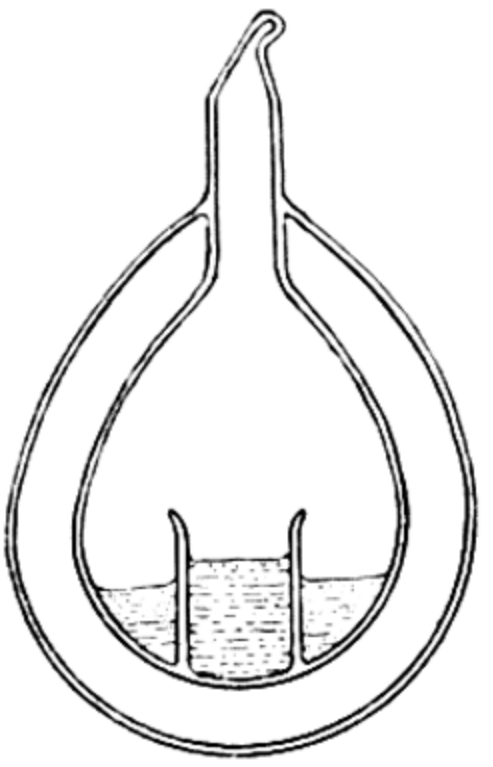


FIG. 4.—Reaction vessel for experiments on the Conservation of Mass.

It follows from the work of Einstein that a change in energy should be accompanied by a change of mass. Chemical changes are often accompanied by the liberation of energy, and if this energy is allowed to leave the system a change in mass should therefore be expected. The change in mass when a gm. molecule (18 gm.) of water is formed from oxygen and hydrogen amounts to about $0{\cdot}3 \times 10^{-8}$ gms., a proportion undetectable by our present weighing instruments, but not beyond the ultimate possibility of detection. Such quantities may be regarded as negligible in even the most accurate chemical work. The mass-equivalent of energy becomes quite important, however, in nuclear changes (Ch. XXVI.) whose energy is very great.

Mass and energy are now to be regarded as to some extent equivalent, and there is a true conservation of mass and energy combined, if not of each singly. According to the work of Einstein, where $m$ and $E$ are equivalent quantities of mass and energy, and C is the velocity of light.

$$E = mC^2$$

**31. The Law of Constant Proportions.**—The Law of Constant Proportions (also known as the Law of Constant Composition or of Definite Proportions) states that **when elements unite together to form chemical compounds they do so in certain fixed proportions,** or, otherwise expressed, **each chemical compound is always composed of the same elements united in the same fixed proportions.**

Thus water always contains 11·19 per cent. of hydrogen and 88·81 per cent. of oxygen; and calcium carbonate 40·05 per cent. of calcium, 11·99 per cent. of carbon, and 47·96 per cent. of oxygen.

This law is not self-evident, and it was only after a considerable controversy at the beginning of the nineteenth century that it was decided that compounds were of unvarying composition. The law may be illustrated and tested by preparing the same compound in several

different ways, and then analysing the several samples obtained.

Thus we may convert copper into black copper oxide: (1) by heating it in oxygen; (2) by dissolving it in nitric acid and heating the nitrate; (3) by heating it in chlorine, dissolving the chloride in water, precipitating the hydroxide, filtering this off and heating it. In each instance 1·0000 gm. of copper forms 1·2517 gms. of the oxide.

A much more cogent proof of this law is the fact that its truth is assumed in all analytical work. Analysis is based on the belief that the composition of compounds is always the same. For example, when we determine silver we precipitate it as chloride, weigh this and calculate the weight of silver as $\frac{107{\cdot}88}{143{\cdot}34}$ of the weight of the chloride, thereby assuming that the latter always contains the same proportion of silver. Now, although analytical results may prove incorrect for many reasons, no errors have yet been traced to the inconstancy of composition of a substance which we have reason to believe is a pure compound. We may conclude then that, within the limits of accuracy possible to experimental work on such a subject, chemical compounds are of constant composition.

**32. Law of Multiple Proportions.**—The Law of Multiple Proportions was discovered by Dalton. It states that **when two elements combine to form more than one compound, the several weights of one element which combine with a fixed weight of the other element are in the ratio of simple whole numbers.**

As examples, we may quote the very careful analyses which have been made of the chlorides of iron.

These analyses have shown that 32·870 gms. of chlorine are contained (1) in 58·866 gms. of ferrous chloride, and (2) in 50·244 gms. of ferric chloride.

It follows then that:

(1) In ferrous chloride 58·866 − 32·870 = 25·996 gms. of iron combine with 32·87 gms. chlorine.

(2) In ferric chloride 50·244 − 32·870 = 17·374 gms. of iron combine with 32·87 gms. chlorine.

Then the same weight of chlorine (32·87 gms.) combines with (1) 25·996 gms. of iron; (2) 17·374 gms. of iron.

Now the numbers 25·996 and 17·374 bear the same ratio as

$$\frac{25{\cdot}996}{17{\cdot}374} \text{ and } 1.$$

$$\text{But } \frac{25{\cdot}996}{17{\cdot}374} = 1{\cdot}497,$$

and the ratio of the weights of iron combined with the same weight of chlorine are as 1 : 1·497, or as 2 : 2·994, which, within the limits of experimental error, may be regarded as the simple proportion 2 : 3.

**33. The Law of Reciprocal Proportions.**—The Law of Reciprocal Proportions marks a further advance. By analysis of the compounds of several elements, it appears that there is not only a regularity apparent in the several proportions in which the same two elements combine to form different compounds; but also in the proportions in which a number of different elements combine to form compounds.

The law of Reciprocal Proportions states that :—

**When two or more elements (A, B, C, etc.) severally combine with another element (D), then the respective weights of these elements (A, B, C, etc.) which combine with a fixed weight of the other (D), are in the same proportions as those in which they combine to form compounds among themselves (AB, AC, BC, etc.), or in simple multiples of these proportions.**

To take a simple case. It is found by analysis that :

(1) 3·00 gms. of carbon combine with 35·46 gms. of chlorine (in carbon tetrachloride).

(2) 3·00 gms. of carbon combine with 8 gms. of oxygen (in carbon dioxide).

(3) 35·46 gms. of chlorine combine with 8 gms. of oxygen in chlorine monoxide, and with 32 gms. in chlorine dioxide.

Thus, if the above law is correct, it follows from results (1) and (2) that the weights 35·46 gms. and 8 gms., being the weights of chlorine and oxygen which combine with a fixed weight of carbon (3 gms.), should give the proportion by weight in which chlorine combines with oxygen, or a simple multiple of that proportion.

Chlorine should then combine with oxygen in the proportion by weight of 35·46 : 8 (or 35·46 : 4, or 35·46 : 16, etc.). The actual ratios from (3) are, in fact, 35·46 : 8, and 35·46 : 32, (4 × 8), and serve to confirm the Law of Reciprocal Proportions.

**34. Equivalent or Combining Weights.**—It follows from the Law of Reciprocal Proportions that if we set down the weights of all the elements which combine with, say, 8 gms. of oxygen, these weights will be in the proportions in which the elements combine with one another (or in simple multiples of such proportions). If we find that[1]

| | |
|---|---|
| 8 gms. of oxygen combine with | 20 gms. calcium.<br>1 gm. hydrogen.<br>28 gms. iron.<br>100 gms. mercury.<br>8 gms. sulphur.<br>35·46 gms. chlorine.<br>23 gms. sodium.<br>108 gms. silver, etc. |

then the numbers in the right-hand column will give the proportions

[1] Most of these numbers are rounded off to whole numbers.

in which these elements combine together. Thus it follows that, for example :—

| | |
|---|---|
| 1 gm. of hydrogen or 108 gms. silver, or any of the weights of the elements given in the previous table will also combine with :— | 20 gms. calcium.<br>28 gms. iron.<br>100 gms. mercury.<br>8 gms. sulphur.<br>35·46 gms. chlorine.<br>23 gms. sodium.<br>8 gms. oxygen.<br>or simple multiples of these. |

The numbers we have given above are called the *combining weights* or *chemical equivalents* of these elements, for they give the proportions in which these elements combine. The quantity of 8 parts by weight of oxygen has been taken as standard of combining weight, because the adoption of this number makes no equivalent less than one, and most equivalents very nearly whole numbers. Moreover, oxygen forms a compound with every element which forms any compounds at all, and is therefore more suitable than an element such as hydrogen, which does not form so wide a range of compounds.

We may then define equivalent or combining weights as follows:—

**The combining weight or chemical equivalent of an element is the number of parts by weight of it which combine with or replace [1] 8 parts by weight of oxygen or the combining weight of any other element.**

The determination of combining weights is of great importance, for it is from the combining weight that the atomic weight is in almost all cases deduced.

**35. Methods of Determining Equivalents or Combining Weights.**—In order to determine the equivalent of an element or compound, we require to know the weight of it which combines with or displaces 8·000 parts by weight of oxygen, 1·008 parts by weight of hydrogen, or the equivalent weight of any other element or compound.

The methods which have been used for this purpose vary considerably, but some of the more important ones are given below.

(1) *Conversion of Element into Oxide.*—A known weight of the element may be converted into the oxide, which is collected and weighed. If the weight of the element used is $w$ gms., and the weight of the oxide formed is $w'$ gms., then $w' - w$ gms. oxygen combine with $w$ gms. of the element, and 8·00 gms. of oxygen combine with $\frac{8w}{w' - w}$ gms. of the element, and its equivalent is $\frac{8w}{w' - w}$.

[1] See § 35 (3), *above*.

(2) *Reduction of Oxide.*—The oxide of the element may be decomposed and the weight of oxygen or of the element or of both directly determined.

Thus the careful reduction of a weighed amount of pure iron oxide by heating it in a current of hydrogen showed that 100·0000 gms. of iron oxide yield 69·9427 gms. iron.

Thus 100 – 69·9427 gms. oxygen combine with 69·9427 gms. iron to form the oxide, and 8·000 parts by weight of oxygen combine with $\frac{69{\cdot}9427 \times 8}{30{\cdot}0573}$ parts by weight of iron = 18.616, and this is the equivalent weight of iron.

(3) *Hydrogen Equivalents.*—If a metal reacts with an acid, displacing hydrogen, then the weight of the metal used becomes combined with the same weight of acid radical as was originally combined with the hydrogen displaced.

$$\text{Metal} + \underset{\text{(acid)}}{[\text{hydrogen} + \text{acid radical}]} = \underset{\text{(salt)}}{[\text{Metal} + \text{acid radical}]} + \text{hydrogen.}$$

Since the hydrogen and the metal in turn combine with the same weight of the acid radical, their weights (by the Law of Reciprocal Proportions) give the weights of metal and hydrogen which would combine with each other if a compound were formed. The equivalent of hydrogen is 1·008, and the equivalent of the metal is, therefore, the weight of it which causes 1·008 gms. of hydrogen to be evolved.

In practice, a weighed amount of the element is allowed to react with excess of a suitable acid, the hydrogen being collected in one of the many well-known forms of gas-measuring apparatus. The volume of hydrogen is corrected (§ 44) to give its true volume as dry gas at 0° C. and 760 mm., and the weight calculated from the fact that 11,200 c.c. of hydrogen weigh 1·008 gms. The method is not accurate enough for modern atomic-weight determinations.

(4) *Determination through Other Elements.*—The equivalent of an element may be determined by converting a weighed amount of it into a weighed amount of its compound with any other element of which the equivalent is known. Thus the equivalent of silver may be determined by heating a weighed portion in a current of chlorine until it is completely converted into silver chloride. The increase of weight gives the weight of chlorine (eq. 35·457) combining with the known weight of silver. The calculation is performed as in Method (1).

(5) *Indirect Methods.*—A method which is much in use is to convert a compound of the element with an element or group of which the equivalent is known, into a compound with another element or group of which the equivalent is known.

Thus let us suppose that in a certain experiment 1·000 gms. of calcium oxide was converted by the action of hydrochloric acid into 1·981 gms. of calcium chloride. The equivalent of oxygen is 8, and of chlorine is taken as 35·46.

Then if the equivalent of calcium is $x$,
$(x + 8)$ gms. of calcium oxide becomes $(x + 35{\cdot}46)$ gms. of calcium chloride,

1 gm. of calcium oxide becomes $\dfrac{x + 35{\cdot}46}{x + 8}$ gms. of calcium chloride.

Thus from the experimental results :—

$$\frac{x + 35{\cdot}46}{x + 8} = 1{\cdot}981$$

$$1{\cdot}981x - x = 35{\cdot}46 - 8 \times 1{\cdot}981$$

$$x = \frac{35{\cdot}46 - 15{\cdot}848}{{\cdot}981}$$

$$= 20{\cdot}012.$$

The equivalent of calcium is therefore 20·012.

## THE ATOMIC THEORY

**36. Dalton's Atomic Theory.**—The fundamental chemical laws discussed in the earlier part of this chapter gave rise to and are explained by the atomic theory. It had been supposed from time to time during the preceding 2,200 years that matter was composed of atoms, and these chemical laws gave a most convincing piece of evidence that matter behaved as if it had an atomic structure.

Dalton's original assumptions, published in 1807, were that :—

(1) Atoms are real separate material particles which cannot be subdivided by any known chemical process.

(2) Atoms of the same element are similar to one another in all respects, and equal in weight.

(3) Atoms of different elements have different properties—weight, affinity, etc.

(4) Compounds are formed by the union of atoms of different elements in simple numerical proportions, such as 1 : 1, 1 : 2, 1 : 3, etc.

These assumptions have had to be modified since Dalton's time, and the part of his work which may be still regarded as valid is comprised in the following statement of the atomic theory in its simplest form.

Every element is made up of atoms which do not undergo subdivision during chemical reactions. The atoms of any one element are constant in weight and exactly alike,[1] but atoms of different elements differ in weight and other properties. Chemical compounds are formed by the union of the atoms of different elements in fixed integral numerical proportions.

The chief piece of evidence available for the atomic theory in Dalton's time was its complete explanation of the fundamental chemical laws, and since his time not only have the facts explained by the atomic theory greatly increased in number, but convincing physical demonstrations (pp. 166 *seq.*) of the real existence of the atoms have placed the theory beyond all reasonable doubt.

**37. Chemical Symbols and Nomenclature.**—Since the atomic theory postulated that all the molecules of each particular compound are made up of the same fixed numbers of the same kind of atoms, it was from the first found convenient to have a simple means of symbolising the numbers and kinds of atoms which make up a particular kind of molecule. Dalton invented a rather clumsy symbolism which was only suited to simple compounds, but this was soon replaced by the modern system in which the atoms of the various chemical elements are represented by symbols derived from the initial letters of the name of the element.

A few examples may be given here, illustrating the way in which these symbols have been derived :—

| Element. | Symbol. |
|---|---|
| Arsenic | As |
| Boron | B |
| Chlorine | Cl |
| Gold | Au (Lat. *aurum*) |
| Iron | Fe (Lat. *ferrum*) |
| Oxygen | O |
| Potassium | K (*Kalium*; Latinised form of Arabic *qaliy*) |
| Tungsten | W (Wolfram) |
| Zinc | Zn. |

A full list of these symbols is given in § 149.

It is important to realise just what these symbols mean. It is often loosely said that Cu is the symbol for copper, or H for hydrogen. Cu does not mean 'copper,' but has the more definite meaning of 'one atom of copper.'

Where reference is made to two or more atoms combined or united in a compound, a subscript figure is added to the symbol.

[1] But see § 148.

Thus $O_2$ means two atoms of oxygen chemically combined. If it is desired to express symbolically two uncombined atoms or molecules, a prefixed figure is used. Thus 2Hg means two atoms of mercury not combined together.

The molecules of compounds are represented by the symbols for the elements which compose them, together with the necessary prefixes or suffixes required to show the number of such atoms.

Thus the formula $Fe_3O_4$ means 'one molecule made up of three atoms of iron and four atoms of oxygen.'

The arrangement of the atoms in the molecule is conveyed by various devices. A bracket is often used to surround a group of atoms which behaves chemically as a single unit, and suffixes and prefixes may be added to such a bracket. Thus $Al_2(SO_4)_3$ means 'one molecule containing two atoms of aluminium and three groups of atoms, each consisting of one sulphur atom and four oxygen atoms.' This way of writing the formula implies that the oxygen and sulphur bear a more intimate relation to each other than they do to the rest of the molecule.

Combination between closely associated groups of atoms is conveyed by separating the formulæ of these by a full stop. Thus alum behaves like a compound of potassium sulphate, aluminium sulphate and water, and its formula is sometimes written—

$$K_2SO_4.Al_2(SO_4)_3.24H_2O.$$

**38. Equations.**—A chemical change is represented by a chemical equation. In addition to the symbols already mentioned, the equation employs the symbol +, which has the meaning of 'reacts with,' and =, which means 'combine, forming an equal weight of.'

The equation

$$H_2 + Cl_2 = 2HCl$$

therefore symbolises the statement that 'when hydrogen and chlorine react, one molecule of hydrogen reacts with one molecule of chlorine forming two molecules of hydrogen chloride.'

The sign $\rightarrow$ is often used in place of =. An equation with the sign $\rightleftharpoons$ represents two simultaneous chemical changes in opposite senses. Thus

$$2Hg + O_2 \rightleftharpoons 2HgO$$

is a more concise way of expressing the two changes

$$2Hg + O_2 \rightarrow 2HgO$$
$$2HgO \rightarrow 2Hg + O_2$$

proceeding simultaneously.

The signs $\uparrow$ and $\downarrow$ are conveniently used to express the fact that

a product of a chemical change is evolved as vapour ( ↑ ) or precipitated ( ↓ ) as an insoluble substance.

Thus the equation—

$$Ca(HCO_3)_2 = CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

means that 'one molecule of calcium bicarbonate decomposes, and forms one molecule of calcium carbonate (which is precipitated), one molecule of water, and one molecule of carbon dioxide (which is evolved as a gas).'

**39. The Atomic Theory and the Fundamental Chemical Laws.**—As has been stated above, the simple assumptions of the atomic theory serve to explain the chemical laws.

(1) *The Conservation of Mass.*—If the atoms are to be considered as indivisible and indestructible,[1] chemical changes consist merely in a rearrangement of these atoms, and no change in mass is to be expected as a result of a mere redistribution of bodies, which are themselves unchanged.

(2) *The Law of Constant Composition.*—The atomic theory assumes that any compound consists of atoms of certain elements united in certain fixed proportions. Suppose that $n$ atoms of the element A combine with $m$ atoms of the element B to form the smallest particle or molecule of a compound $A_nB_m$. Then, if an atom of the element A weighs $a$ gms., and an atom of the element B weighs $b$ gms., the molecule of the compound weighs $na + mb$ gms. and the proportion of the elements A and B in the compound are $\frac{na}{na+mb}$ and $\frac{mb}{na+mb}$ respectively. According to the atomic theory, $m$ and $n$ are fixed for any one compound, while $a$ and $b$ are also invariable quantities. It follows, then, that the above fractions, representing the proportions by weight of the various elements in the compounds, are fixed and invariable.

(3) *The Law of Multiple Proportions.*—Suppose that two elements A and B form three different compounds. According to the atomic theory these must contain different numerical proportions of A and B atoms. Suppose they are (1) $A_cB_d$ ; (2) $A_nB_m$ ; (3) $A_xB_y$. Then the proportions by weight of the elements A and B will be :—

(1) $ca : db$ i.e., $a : \frac{d}{c}b$.

(2) $na : mb$ i.e., $a : \frac{m}{n}b$.

(3) $xa : yb$ i.e., $a : \frac{y}{x}b$.

[1] But see p. 26, also Ch. XXVI., *passim*.

where $a$ and $b$ are the weights of an atom of A and B respectively.

The weights of the element B combined with a fixed weight ($a$) of the element A, are, therefore, $\frac{db}{c}$, $\frac{mb}{n}$, $\frac{yb}{x}$. And these are in the proportion

$$\frac{d}{c} : \frac{m}{n} : \frac{y}{x},$$

i.e., $dnx : mcx : ycn$.

Now $c$, $d$, $m$, $n$, $x$, $y$, are whole numbers, since they represent the numbers of atoms in the molecule of a compound, and so their products are also whole numbers. It follows, then, that where two elements (A, B) form several compounds ($A_cB_d$, $A_nB_m$, $A_xB_y$), the weights of one element (B) which combine with a fixed weight ($a$) of the other element (A), are in a proportion represented by small integers ($dnx$, $mcx$, $ycn$), and this is what the law of multiple proportions asserts.

(4) *Law of Reciprocal Proportions.*—Suppose that the elements A, B, C, whose atoms weigh respectively $a$, $b$, $c$ gms., form several compounds, which, according to the atomic theory we may regard as being made up of molecules containing fixed numbers of A, B and C atoms, *e.g.*, $A_nB_m$, $B_pC_q$, $A_xC_y$. Then, according to the law of reciprocal proportions, the weights of the elements B and C, which combine with the same fixed weight of the element A, should give the proportions by weight in which B and C combine or simple multiples of these proportions.

The proportion by weight of A to B in their compound $A_nB_m$ is

$$na : mb$$

or

$$a : \frac{mb}{n},$$

The proportion by weight of A to C in their compound $A_xC_y$, is

$$xa : yc$$

or

$$a : \frac{yc}{x}.$$

Then, according to the law of reciprocal proportions, B and C should combine in the proportion

$$\frac{mb}{n} : \frac{yc}{x}$$

or in some simple multiple or submultiple of this proportion.

If B and C form a compound $B_pC_q$, then the proportions of these elements by weight will be $pb : qc$.

Now if $m$, $n$, $x$, $y$, $p$, $q$, are all small whole numbers as the atomic

theory states, the proportion $\frac{m}{n} : \frac{y}{x}$ must be simply related to the proportion $p : q$. If the simplest compounds of A, B, and C are selected, it often happens that $m$, $n$, $x$, $y$, $p$, $q$ are all equal to unity, in which case the proportions are identical.

The atomic theory then gives a complete explanation of the fundamental chemical laws, and almost the whole of our chemical theory is based upon it. Subsequent discoveries have greatly enlarged our knowledge of the atom, and Chapter VII. contains some account of the more recent knowledge about its remarkable structure and behaviour.

# CHAPTER III

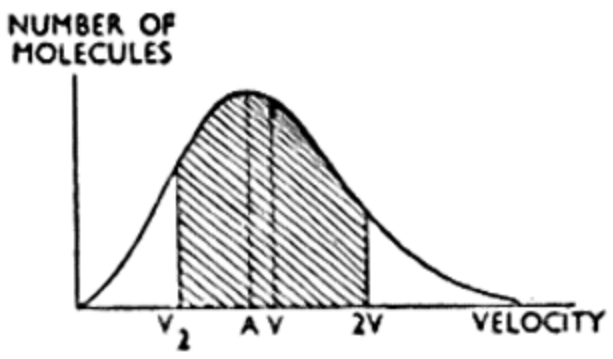
## MOLECULAR AND ATOMIC WEIGHTS

### The Kinetic Theory.

**40. Molecular Motion.**—The simple form of the Atomic Theory, as derived from the fundamental chemical laws discussed in the last chapter, led to a belief that matter had a discontinuous or atomic structure. It led, however, to no knowledge of the way the ultimate particles of matter were arranged in space. The discovery of the nature of the motions of these particles is a matter to be classified as Physics rather than Chemistry, and it will be enough to state the conclusions reached.

According to the kinetic theory matter of every kind under all realisable conditions is made up of particles—molecules—which are in rapid motion. The velocity of the particles is greater as their mass is less, and an increase of temperature involves and, in fact, consists in an increase of this velocity. The character of the motion is different in the cases of solids, liquids and gases.

**41. The Nature of Gases, Liquids and Solids.**—A gas consists of an assemblage of molecules in rapid and chaotic motion. The distance between the molecules, of course, varies continuously, but the average distance between the molecules is very much greater than the diameter of a single molecule (about 370 times in the case of oxygen at N.T.P.). This distance is expressed by the *mean free path*, which is the average distance a molecule will travel before it collides with another. The individual molecules in any mass of gas have not the same velocity, which in fact varies between zero and very high values. Most of the molecules have velocities round about the average value, but a proportion move more slowly and a proportion more rapidly. The curve in Fig. 5 expresses the connection between the velocity of the molecules and the number of molecules having that velocity.




A. average velocity of molecules in gas
V. root-mean-square velocity.

Fig. 5

If we call the *root-mean-square*[1] velocity $v$ then most of the mole-

[1] The root-mean-square velocity is the square root of the average of the squares of the velocities of the separate molecules. It is about 8 per cent. greater than the average.

cules have a velocity not far from this value ; thus the shaded area in Fig. 5 represents the molecules whose velocities are not more than half or twice the root-mean-square. It is to be noted, however, that some few molecules are moving much more rapidly, up to two or three times the root-mean-square value, while a few are moving much more slowly.

The actual figures for oxygen at 0° C. and 760 mm. are given below.

| | |
|---|---|
| Number of molecules per litre | $= 2{\cdot}8 \times 10^{22}$ |
| Average velocity | $= 4{\cdot}1 \times 10^{4}$ cm./sec. (1342 ft./sec.) |
| Mean free path | $= 0{\cdot}00001$ cm. |
| Diameter of an oxygen molecule | $= 2{\cdot}7 \times 10^{-8}$ cm. |
| Number of collisions undergone by each molecule | = 5,780,000,000 per sec. |

*Liquids.*—The same type of chaotic motion takes place in both liquids and gases, but the molecules of liquids are far closer together than are those of gases. The mean free path of a molecule of liquid is not much more than its own diameter. The molecules are, in fact, close enough to be held together by their mutual attraction.

*Solids.*—In solids the molecules are in continual vibratory motion about fixed centres and, although the molecules do not wander from their fixed arrangement, they influence each other by molecular attraction. The solid state is discussed in more detail in §§ 98–103.

**42. Temperature.**—According to the kinetic theory the temperature of a body is proportional to the mean kinetic energy of translation[1] of the molecules. Thus, if the root-mean-square velocity of the molecules is $u$ and the mass of the molecules $m$, the mean kinetic energy of the mass of gas is $\frac{1}{2}mu^2$. An increase of velocity brings about an increase of temperature and *vice versa*. It follows that if the molecules are caused to lose energy (cooled) the process will cease when no energy is left and $\frac{1}{2}mu^2 = 0$. This will occur when the molecules are at rest and it is calculated that this condition of rest would correspond to a temperature of − 273·2° C., *absolute zero*. This temperature has never been reached, but the lowest value attained is only 0·0044° above it. It would seem impossible in practice to reach the absolute zero, for this would imply reducing every single molecule in the substance cooled to a condition of rest and allowing no moving molecule to come into contact with it.

[1] Kinetic energy due to the linear motion of the molecule as a whole as distinguished from kinetic energy due to rotation, internal motions, etc.

Pratap College,

## The Gas Laws and the Kinetic Theory.

**43. Boyle's Law and Charles' Law.**—Of considerable importance to chemical theory are Boyle's law and Charles' law, which define the relationship between the volume, pressure and temperature of a mass of gas.

Boyle's law states that **if the temperature of a mass of gas remains constant, its volume varies inversely as the pressure upon it.**

Expressed mathematically, Boyle's law states that if $p$ is the pressure upon a gas and $v$ is its volume, then $pv$ is a constant, or $pv = k$.

The experimental proof of this is to be found in text-books of physics, and the law is found to express the facts accurately where very high pressures are not in question and where the gas is well above its liquefaction temperature. If we assume the truth of the kinetic theory Boyle's law may be proved theoretically.

The following proof is not quite rigid, but gives a good idea of the general principle. Consider a mass of gas of volume $v$ and pressure $p$ and mass M and suppose that one cubic centimetre of this gas is contained in a cubical vessel of 1 cm. side and contains $n$ molecules, each of velocity $u$ and mass $m$.

Since the velocity of the molecules is $u$ cm. per second, each molecule collides with a wall of the cube, on an average, $u$ times per second. Its momentum, when it rebounds, changes from $+ mu$ to $- mu$, and the total change is $2mu$ per collision, and therefore $2mu^2$ is the total change of momentum per second. Now Pressure $= \frac{\text{Force}}{\text{Area}}$ and force is measured by the rate of change of momentum. Thus the change of momentum of the molecules impinging on unit area in unit time gives the pressure. We have imagined the pressure due to this change as distributed over two walls of the cube. If we imagine $n$ molecules in the space within the cube, $\frac{n}{3}$ of these may be regarded as travelling between each pair of walls and exerting a pressure due to their change of momentum of $\frac{2}{3}.nmu^2$. Considering the impacts on one single wall, the pressure will be $\frac{1}{3}mnu^2$,

But $nm$ = the mass of the gas in a unit cube, which is equal to the density $\rho$

$$\therefore \quad p = \tfrac{1}{3}\rho u^2$$

but
$$\rho = \frac{\mathrm{M}}{v}$$

$$\therefore \quad pv = \tfrac{1}{3}\mathrm{M}u^2.$$

But if the temperature is constant the kinetic energy of the molecules $\frac{1}{2}mu^2$ is constant and $\frac{1}{3}\mathrm{M}u^2$ is also constant.

and
$$pv = \text{a constant } (k).$$

This proof assumes that the molecule is infinitely small compared with its free path, and also that the molecules have no mutual attraction or repulsion. Neither of these assumptions is true, but at the pressures usually handled in the laboratory the effects of these slight inaccuracies are negligible. With

gases at very high pressures and also with gases near their temperature of liquefaction these inaccuracies become comparatively large. Thus, if we consider a mass of nitrogen such that $pv = 1$ at N.T.P., then at 100 atmospheres pressure $pv = 0{\cdot}991$, at 400 atm. 1·257, at 1,000 atm. 2·0685.

The following table shows the character of the deviations from Boyle's law in the case of a gas near its point of liquefaction, namely carbon dioxide at 50° C.

| Pressure in atmospheres | $pv$. |
|---|---|
| 1 | 1·183 |
| 50 | 0·920 |
| 100 | 0·491 |
| 125 | 0·395 |
| 150 | 0·419 |
| 400 | 0·852 |
| 600 | 1·187 |
| 1,000 | 1·814 |

As the pressure is increased all gases, except hydrogen and helium, at first diminish in volume more than Boyle's law predicts. This phenomenon is due to the attraction of the molecules for each other. At very high pressures the gases contract less than would be expected owing to the fact that the actual molecules are taking up a large part of the total volume of the gas and the space for contraction is thereby diminished. Several revised gas laws have been put forward by Van der Waals, Dieterici and others, which make allowance for these changes by introducing two or more constants.

*Charles' Law* (Gay-Lussac's Law).—The relation between the temperature ($t$) and volume ($v$) of a gas is given by this law, which states that if the pressure of a given mass of gas be kept constant, the volume varies directly as the absolute temperature. We may express this as

$$\frac{V}{T} = \text{constant.}$$

*General Expression of the Gas Laws.*—Boyle's law and Charles' law may be combined in the important expression

$$\frac{PV}{T} = \text{constant}$$

where P, V, and T are the pressure, volume and temperature of any mass of gas.

**44. Correction of Volumes of Gases for Temperature and Pressure.**—It is frequently required in chemical operations to find the volume of a mass of gas at some given temperature and pressure, its volume being known under different conditions. This is easily accomplished by means of the above expression. If a mass of gas has a volume $V_0$ under a pressure $P_0$ at an absolute temperature $T_0$, and a volume $V_1$ under a pressure $P_1$ at a temperature $T_1$,

Then $$P_0V_0 = T_0 \times k$$

and $$P_1V_1 = T_1 \times k.$$

$\therefore$ $$\frac{P_0V_0}{T_0} = \frac{P_1V_1.}{T_1}$$

*Example.*—Some oxygen measured at 10° C. and 730 mm. pressure has a volume of 15·50 c.c. What would be its volume at 0° C. and 760 mm. pressure ?

$P_0 = 730$ mm. $V_0 = 15{\cdot}5$ c.c. $T_0 = 283°$ A.

$P_1 = 760$ mm. $V_1 =$ ? $T_1 = 273°$ A.

$$\frac{730 \times 15{\cdot}5}{283} = \frac{760 \times V_1}{273}$$

$$V_1 = \frac{730 \times 15{\cdot}5 \times 273}{283 \times 760}$$

$$= 14{\cdot}36 \text{ c.c.}$$

The volumes of gases are almost always expressed as the volume at standard temperature and pressure (S.T.P. or N.T.P.) which is the volume which the dry gas would assume at 0° C. and 760 mm. pressure.

**45. Gay-Lussac's Law.**—A remarkable fact which was first stated by Gay-Lussac in 1808 is that *when gases react they do so in simple proportions by volume.*

Thus 1 volume of oxygen unites with precisely 2 volumes of hydrogen forming water ; 2 volumes of ammonia gas react with 3 volumes of chlorine.

The above statement is known as Gay-Lussac's law and is accounted for by Avogadro's law and the Atomic Theory. When molecules react, they do so in the proportion of small whole numbers, as is indicated by the use of chemical equations to express such changes. So suppose that $a$ molecules of gas A react with $b$ molecules of gas B and that under the conditions of temperature prevailing 1 c.c. of each gas contains N molecules.

$a$ molecules of gas are contained in $\frac{a}{N}$ c.c. of gas A.

$b$ molecules of gas are contained in $\frac{b}{N}$ c.c. of gas B.

The reacting volumes are therefore $\frac{a}{N}$ c.c. and $\frac{b}{N}$ c.c. and are related as $a$ is to $b$, both of which are small whole numbers.

**46. Gas Densities and Avogadro's Hypothesis.**—Early in the nineteenth century it was noticed that there was a connection between the density of a gas and its formula, but the uncertainty about the atomic weights and formulæ which prevailed up to about 1850

made it difficult to define what the true relationship was. Avogadro, in 1811, put forward a hypothesis, which, owing to the difficulty of reconciling it with the formulæ and atomic weights then in use, was not adopted until Cannizzaro brought it to light again in 1858 in his "Sketch of a Course of Chemical Philosophy."

This hypothesis, which is the basis of a great part of chemical theory, was to the effect that

**Equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules.**

For if, by Dalton's atomic theory, a molecule of one element reacts with a small, whole number of molecules of another element, and if, by Gay-Lussac's law, the elements when gaseous react in simple proportions by volume, then it would appear, as Avogadro thought, that equal volumes of gases under the same conditions would contain the same number of molecules. Thus the hypothesis is a derived consequence of Dalton's atomic theory and Gay-Lussac's law.

This may be deduced from the kinetic theory as stated above.

Let two equal volumes of two different gases contain respectively $n$ and $n_1$ molecules in unit volume and let the masses and root-mean-square velocities of these molecules be $m$, $m_1$, and $u$, $u_1$. Both gases are at pressure $p$, so

$$p = \tfrac{1}{3}nmu^2$$

and

$$p = \tfrac{1}{3}n_1m_1u_1^2,$$

and so

$$nmu^2 = n_1m_1u_1^2 \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Since the gases are at the same temperature the kinetic energies of their molecules are the same, and

$$\tfrac{1}{2}mu^2 = \tfrac{1}{2}m_1u_1^2 \quad . \quad . \quad . \quad . \quad . \quad (b)$$

And by dividing equation ($a$) by equation ($b$)

$$n = n_1,$$

which is the assertion of Avogadro's hypothesis.

**47. Relative Density of Gases and Molecular Weights.**—With the help of Avogadro's law it is easy to arrive at the *molecular weight* of any substance which can be brought into the gaseous state.

From the molecular weights of compounds it is possible to arrive at the atomic weight of elements, and thence to derive our whole system of chemical formulæ. The only measurements required are the determination of the *mass* and *volume* of a mass of gas or vapour under known conditions of *temperature* and *pressure*.

Before discussing the methods of determining these quantities it will be as well to define them in order to be sure that the reader knows exactly what is meant by the terms to be used.

*The Atom* is the smallest[1] particle of any particular element which can take part in a chemical change.

[1] The electron, though a smaller particle, cannot be called a particle of any particular element. An "electron of sulphur" would be a meaningless expression.

*The Molecule* is the smallest particle of a particular form of an element or compound which can exist in the free state.

*The Atomic Weight* of an element is the ratio of the weight of its atom to the weight of an atom of hydrogen (or to one-sixteenth of an atom of oxygen).

*The Molecular Weight* of an element or compound is the ratio of the weight of one molecule of it to the weight of an atom of hydrogen.

*The Density of a Gas relative to Hydrogen* is the ratio of the weight of a volume of a gas to the weight of the same volume of hydrogen under the same conditions of temperature and pressure.

The gram-molecular weight and gram-atomic weight are the molecular and atomic weights respectively, expressed in grams.

**48. Molecular Weight of Hydrogen.**—In order to find out the connection between gas densities and molecular weights it is necessary, as will be seen, to discover the molecular weight of *one* gas.

We have called the atomic weight[1] of hydrogen 1, and its molecular weight is therefore $n \times 1{\cdot}000$ if the molecule of hydrogen contains $n$ atoms and its formula is $H_n$. To find the molecular weight of hydrogen it is therefore necessary to find out its *atomicity*, the number of atoms in its molecule.

The problem of the discovery of the number of hydrogen atoms in the hydrogen molecule was solved by Amedeo Avogadro in 1811. As has already been mentioned, his work was rejected at first, largely because the experimental values for gas densities, etc., current in 1811 were inaccurate and therefore did not agree with his conclusions. His conclusions were revived and shown to be correct by Cannizzaro in 1858.

It is well known that hydrogen combines with numerous elements and forms many gases and volatile hydrides which consist only of hydrogen and the element in question.

Let us suppose that the formula of hydrogen is $H_x$ and the symbol of the element it combines with is A. The formula of the hydride may be (1) $HA_n$, (2) $H_2A_n$, (3) $H_3A_n$, etc.

Let us write the equation in the first case

$$H_x + xnA = xHA_n.$$

One molecule of hydrogen forms $x$ molecules of the hydride.

∴. By Avogadro's Law,

One volume of hydrogen forms $x$ volumes of the gaseous hydride.

In the second case the equation is

$$H_x + \frac{x}{2}.\, nA = \frac{x}{2} H_2A_n.$$

[1] The system of making oxygen the standard with an atomic weight of 16·000 is now adopted, in which case hydrogen has atomic weight 1·008. If the last value be substituted for 1·000 in the above argument, it remains true.

In this case 1 volume of hydrogen will form $\frac{x}{2}$ volumes of hydride. Similarly, if the formula of the hydride were $H_mA_n$, one volume of hydrogen would form $\frac{x}{m}$ volumes of the hydride.

So it follows that the *greatest number of volumes of any hydride obtainable from one volume of hydrogen is equal to the number of atoms in the hydrogen molecule.*

So our problem is now to find experimentally how many volumes of various hydrides can be formed from one volume of hydrogen.

We may consider the practical technique in the case of chlorine.

When hydrogen and chlorine are mixed and subjected to heat (as by an electric spark) they combine with explosion, forming the gas hydrogen chloride. This may be proved experimentally by filling a strong and narrow glass tube (Fig. 6), provided at each end with stopcocks, with a mixture of hydrogen and chlorine in equal volumes. On passing a spark by means of the sealed-in platinum

FIG. 6.—Explosion tube for mixture of hydrogen and chlorine.

wires the mixture explodes, and after cooling, a stopcock may be opened under mercury, when gas is not expelled nor is mercury drawn in, showing that no change of volume has occurred. That hydrogen chloride has actually been formed may be demonstrated by opening the tube under water, when the very soluble gas dissolves and water fills the tube completely. In this way it may be demonstrated that *one* volume of hydrogen and *one* volume of chlorine combine, forming *two* volumes of hydrogen chloride. Many other cases have been studied and some of their results are given in the table on page 54.

In no case yet studied does one volume of hydrogen produce more than two volumes of hydride, so we conclude that the formula of hydrogen is $H_2$.

As a confirmation of the above proof the following argument is often given.

From the results of the experiment described above it follows that one volume of hydrogen and one volume of chlorine form two volumes of hydrogen chloride.

Let us suppose that one volume of hydrogen contains $n$ molecules

of hydrogen. Then by Avogadro's law one volume of chlorine under the same conditions also contains $n$ molecules and two volumes of hydrogen chloride contain $2n$ molecules.

Thus $n$ molecules of hydrogen + $n$ molecules chlorine form $2n$ molecules of hydrogen chloride; and 1 molecule of hydrogen + 1 molecule of chlorine form 2 molecules of hydrogen chloride.

Now each molecule of hydrogen chloride contains some hydrogen, and the quantity contained cannot be less than one atom. The hydrogen in *two* molecules of hydrogen chloride comes from *one* molecule of hydrogen, and so *a molecule of hydrogen contains twice as many atoms of hydrogen as a molecule of hydrogen chloride.*

| Volume of element | Volume of hydrogen | Volume of hydride | Volume of hydride formed from 1 volume of hydrogen |
|---|---|---|---|
| 1 vol. chlorine | + 1 vol. hydrogen | → 2 vols. hydrogen chloride | 2 vols. |
| 1 vol. bromine vap. | + 1 vol. hydrogen | → 2 vols. hydrogen bromide | 2 „ |
| 1 vol. iodine vap. | + 1 vol. hydrogen | ⇀↽ 2 vols. hydrogen iodide | 2 „ |
| Sulphur vapour | + 1 vol. hydrogen | ← 1 vol. hydrogen sulphide | 1 vol. |
| 1 vol. oxygen | + 2 vols. hydrogen | → 2 vols. steam | 1 „ |
| 1 vol. nitrogen | + 3 vols. hydrogen | ↽⇀ 2 vols. ammonia | $\frac{2}{3}$ „ |
| Carbon | + 1 vol. hydrogen | ← 1 vol. acetylene | 1 „ |
| Carbon | + 2 vols. hydrogen | ← 1 vol. methane | $\frac{1}{2}$ „ |

Hydrogen chloride is an acid, and it is characteristic of acids that the hydrogen they contain may be replaced (p. 197) by metals. It is also possible to replace this hydrogen partly or wholly. Now, if hydrochloric acid had the formula $H_nCl_m$ we could prepare from it $n$ sodium compounds, such as $NaH_{n-1}Cl_m$ $Na_2H_{n-2}Cl_m$ . . . $Na_{n-1}HCl_m$, $Na_nCl_m$. (Cf. p. 206.)

Now it is actually possible to prepare *only one* sodium salt of hydrochloric acid (common salt), and there can, therefore, only be *one* hydrogen atom in the hydrochloric acid molecule to be replaced. But the hydrogen molecule contains twice as many atoms of hydrogen as the hydrogen chloride molecule, and its formula is therefore $H_2$.

There is also some physical evidence that hydrogen is $H_2$. Thus the ratio of its specific heats at constant volume and constant pressure is 1·4, a value which indicates a diatomic gas.

**49. Molecular Weight of Gases other than Hydrogen.**—The molecular weight of hydrogen is known to be 2; for the atomic weight of hydrogen is assumed to be 1, as standard of atomic weight,[1]

[1] If the oxygen standard O = 16 is adopted, the figure 1·008 for the atomic weight and relative density of hydrogen and 2·016 for its molecular weight are to be substituted in the above arguments.

and the arguments adduced in § 48 show that the molecule of hydrogen contains two atoms. The gram-molecular weight of hydrogen is therefore 2 gms. Now it may be shown by an experimental determination of the density of the gas that 2 gms. of hydrogen at N.T.P. occupy a volume of 22·412 litres.

Suppose that 22·412 litres of hydrogen contain $n$ molecules of hydrogen. Then by Avogadro's law 22·412 litres of any other gas contain $n$ molecules of that gas.

Suppose that 22·412 litres of this gas, measured at S.T.P., weigh $w$ gms. Then each molecule weighs $\frac{w}{n}$ gms.

But a molecule of hydrogen weighs $\frac{2}{n}$ gms.

$$\therefore \frac{\text{The weight of a molecule of the gas}}{\text{The weight of a molecule of hydrogen}} = \frac{w}{n} \div \frac{2}{n} = \frac{w}{2}.$$

But the weight of an atom of hydrogen is half the weight of a molecule of hydrogen.

$$\therefore \frac{\text{The weight of a molecule of the gas}}{\text{The weight of an } \textit{atom} \text{ of hydrogen}} = w.$$

It follows that **the molecular weight of a gas is numerically equal to the weight in grams of 22.412 litres of the gas measured at N.T.P.**

**50. Gas Density.**—The relative density of a gas referred to hydrogen is the ratio of the weight of one volume of gas to the weight of one volume of hydrogen, both measured at N.T.P.

Using the same symbols as above,

$$\text{Gas density} = \frac{\text{Weight of 22·4 litres of gas at N.T.P.}}{\text{Weight of 22·4 litres of hydrogen at N.T.P.}} = \frac{w}{2}.$$

We have shown that the molecular weight of the gas is $w$ and consequently

**The molecular weight of a gas is twice the relative density of the gas at N.T.P. referred to hydrogen as unity.**

**51. Determination of the Molecular Weight of a Permanent Gas.**—To find the molecular weight of a gas we require to know the weight of a given volume of it at N.T.P. It is very difficult to conduct the experiment under these conditions, and in practice a known volume of the gas ($v$ c.c.) is weighed (weight = $w$ gms.) at a known temperature $t°$ C. and known pressure $p$ mm. of mercury. The volume of the gas at N.T.P. is then $v \times \frac{273}{273+t} \times \frac{p}{760}$ and the weight of 22·4 litres

of it at N.T.P. is $\frac{w \times 22{,}400 \times (273 + t) \times 760}{v \times 273 \times p}$ gms. This quantity is the gram-molecular weight.

The practical details of an experiment of this kind vary enormously according to the degree of accuracy required. The difficulties arise from the fact that a mass of gas is always very light compared with the weight of its container.

Some of the precautions required for accurate weighings of this

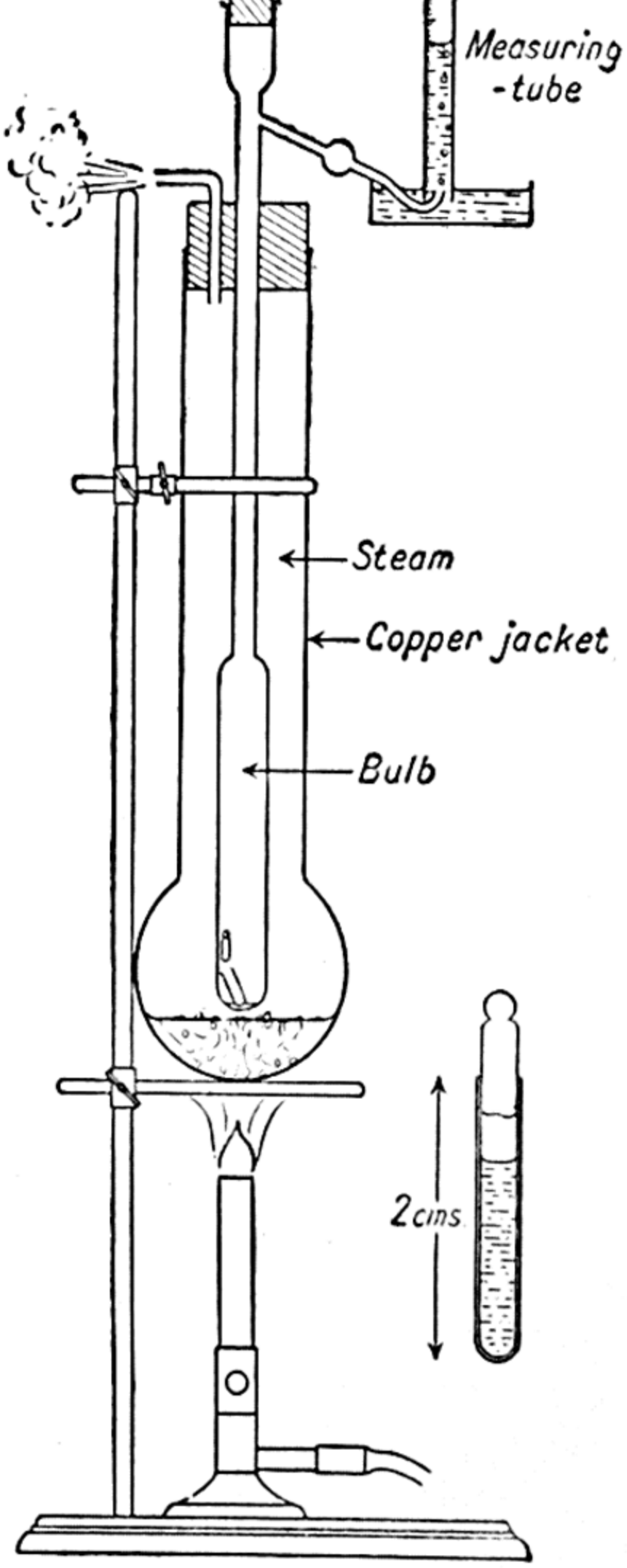



FIG. 7.—Victor Meyer's apparatus for the determination of the density of a vapour.

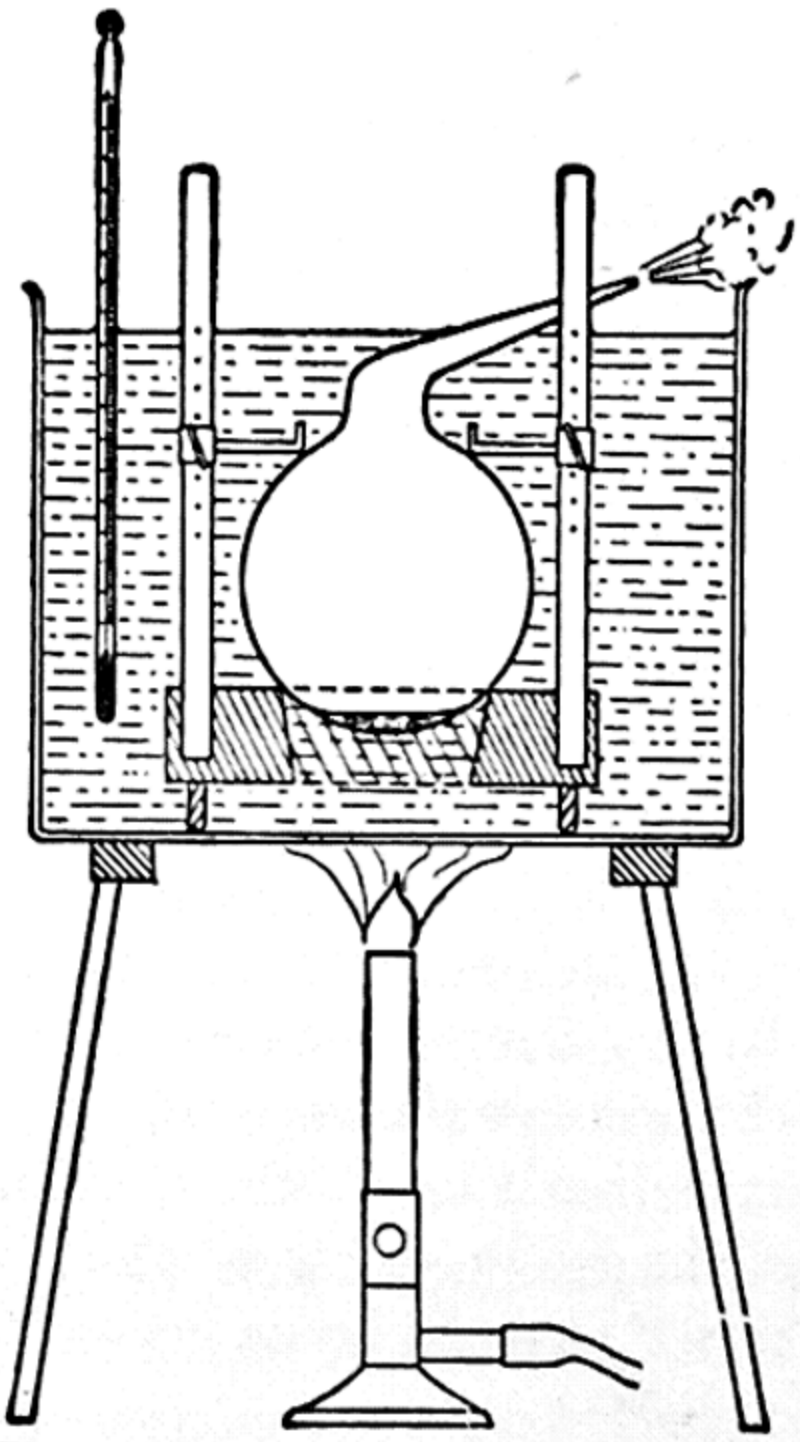


FIG. 8.—Dumas' method for the determination of the density of a vapour.

kind are described in § 69 on the atomic weight of hydrogen.

An example of the method of calculating the molecular weight of a gas from its weight and volume may here be given.

*Example.—An evacuated vessel weighed against a counterpoise and then filled with oxygen at* 16° *C. and* 740 *mm. pressure and weighed again, gained in weight by* 0·4663 *gm. The volume of the vessel was found to be* 354·9 *c.c.*

0·4663 gm. of oxygen occupies 354·9 c.c. at 16° C. and 740 mm.

$\therefore$ At 0° C. and 760 mm. $354{\cdot}9 \times \frac{740}{760} \times \frac{273}{289}$ c.c. is the volume of 0·4663 gm. of oxygen.

$\therefore$ 22·4 litres in the volume of $\frac{0{\cdot}4663 \times 22400 \times 760 \times 289}{354{\cdot}9 \times 740 \times 273}$ gm. oxygen at N.T.P. = 32·0 gms.

$\therefore$ the molecular weight of oxygen is 32.

**52. Molecular Weight of Volatile Liquids and Solids.**—The principle of the method described above may be applied not only to permanent gases but also to volatile liquids or solids, which far exceed the gases in number. Direct weighing of a fixed volume of gas is a method obviously unsuitable for finding the density of a vapour which condenses at room temperature, and for these several other methods have been devised. Among these the methods of Victor Meyer, Dumas and Hofmann are of conspicuous importance.

*Victor Meyer's Method of Determining Molecular Weights.*—In order to discover the molecular weight of a volatile compound it is necessary to convert it into vapour and measure the weight, volume, temperature and pressure of this vapour. In the Victor Meyer apparatus the vapour produced by the evaporation of a known weight of liquid is made to displace its own volume of air which is measured under known conditions. The apparatus is that shown in Fig. 7. A very small bottle is weighed, filled with the volatile liquid and weighed again, thus obtaining the weight ($w$) of liquid used. The jacket is partly filled with a liquid with a boiling point some 30°–40° higher than that of the substance to be vaporised. The liquid in the jacket is set boiling and the tube is stoppered. When air has ceased to issue from the delivery tube, the measuring tube is set over its orifice, the stopper removed and the bottle dropped into the bulb. The stopper is at once replaced. The liquid in the bottle vaporises and forms a vapour at the temperature of the hot jacket. This displaces its own volume of hot air, which passes into the graduated tube and then contracts to a volume ($v$) identical with the volume the vapour would have at the temperature ($t$) and pressure ($p$) prevailing in the graduated tube. None of the vapour reaches the cool part of the tube, for the vapour is of sufficient volume to fill only a part of the inner bulb, and is always a good deal heavier than air.

The volume of the vapour measured at N.T.P. is then

$$\frac{273pv}{(273 + t)\ 760} \text{ c.c.}$$

The weight of the vapour is $w$ gms.

The gram-molecular weight is equal to the weight of 22,400 c.c. of the vapour at N.T.P. (§ 49)

$$\frac{273pv}{(273 + t)\ 760}\ \text{c.c. of the vapour at N.T.P. weigh } w \text{ gms.}$$

$$\therefore\ 22{,}400\ \text{c.c. weigh } \frac{w \times 22{,}400\ (273 + t)\ 760}{273pv}\ \text{gms.,}$$

and this latter figure is the gram-molecular weight.

*Dumas' Method of Determining Molecular Weights.*—The principle of this method is the weighing of a volume of vapour measured at an elevated temperature. The apparatus is shown in Fig. 8. A large bulb with a long pointed neck is weighed ($w_1$). It is then warmed and the orifice dipped into the liquid of which the vapour density is to be determined. When some 10–12 c.c. of the latter have been drawn into the bulb, it is removed and clamped under water (or other liquid) so that only the point protrudes. The water is heated until the liquid boils rapidly and is then kept at a constant temperature $t$, measured by a thermometer in the bath. When no liquid remains in the bulb (as shown by vapour ceasing to issue) the orifice is sealed without removing the bulb from the bath. It is now full of vapour at the temperature ($t$) of the bath and the prevailing atmospheric pressure ($p$). The bulb is now removed, dried, allowed to cool and weighed (weight of the bulb full of vapour $= w_2$).

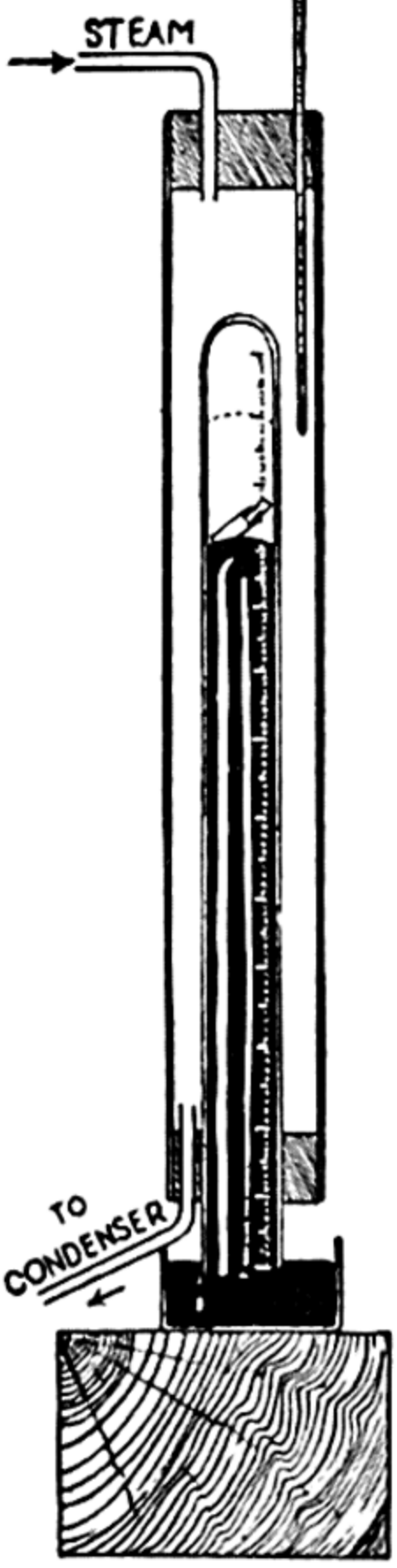



FIG. 9.—Hofmann's method for the determination of the density of a vapour.

The volume of the bulb is next determined by opening it under water which rushes in and fills it. By weighing the bulb so filled its volume $v$ is easily obtained.

The weight of the vapour is $w_2 - w_1 + vd$, where $d$ is the density of air (referred to water) at the temperature and pressure at which the bulb was weighed. The term $vd$ is introduced to allow for the buoyancy of the sealed bulb, which appears less in weight by the weight of the volume of air it displaces.

The volume of the vapour is $v$ at a temperature $t$ and pressure $p$. The calculation is performed as in Victor Meyer's method.

*Hofmann's Method*, which will not be described in detail, consists in allowing a bottle (as in Fig. 9) containing $w$ gms. of a volatile substance to rise into a graduated barometer tube maintained by a jacket at $t°$ C. On vaporisation of the substance the mercury falls, the vapour occupying a volume indicated by the graduations as $v$ c.c. The pressure $p$ is given by the difference between the height of the mercury column and the height of the barometer. The quantities $w$, $v$, $p$, $t$ being known, the molecular weight is calculated as before. The chief experimental precautions are to be directed towards the thorough drying of the mercury and tube.

**53. Diffusion of Gases.**—An entirely different method of determining gas densities is based on the phenomenon of *diffusion*.

Diffusion takes place in both liquids and gases, and to some extent also in certain solids. If a jar of hydrogen be placed mouth downward over a jar of oxygen the lighter gas does not remain on top of the heavier one. The molecules, continually in chaotic motion, become mixed, and after a lapse of time the gas becomes uniform in composition throughout. Liquids and solids in solution diffuse in the same way but more slowly. A piece of copper sulphate dropped into a beaker of water will dissolve and slowly diffuse upward; but if the beaker be kept at constant temperature (to avoid convection currents) it will be months before the copper sulphate is evenly distributed through the water. Even solids diffuse to some extent. Gold will diffuse into lead and carbon into iron, but most solids diffuse only to an immeasurably small extent, if at all.

The rate of diffusion of gases was first studied by Graham. He did not study the rate at which two gases mix, but rather the rate at which gases will pass through a partition of porous material such as pipe-clay or porous earthenware. Graham found that *the relative speeds of diffusion of gases are inversely proportional to the square roots of their respective densities.*

Thus, if 100 c.c. of oxygen (relative density 16) passed through a porous pot in a given time, then $\frac{100 \times \sqrt{16}}{\sqrt{1}}$ c.c. $= 400$ c.c. of hydrogen (relative density 1) would pass through the same pot in the same time under the same conditions.

That this must be so, can be seen from the kinetic theory.

The kinetic energy of all molecules at the same temperature is the same, $\frac{1}{2}mv^2$.

$\therefore$ if two molecules have masses $m_1$, $m_2$, and velocities $v_1$, $v_2$,

$$\tfrac{1}{2}m_1v_1^2 = \tfrac{1}{2}m_2v_2^2$$

$$\therefore \quad \frac{m_1}{m_2} = \frac{v_2^2}{v_1^2}.$$

Equal volumes of gases contain the same number (say $n$) molecules and the weights of equal volumes of these gases are therefore $nm_1$, $nm_2$. But the weight of a given volume is the density of a gas

$$\frac{nm_1}{nm_2} = \frac{v_2^2}{v_1^2}$$

$$\therefore \quad \frac{d_1}{d_2} = \frac{v_2^2}{v_1^2}.$$

Consider a porous vessel with a number of minute apertures each ·001 mm. in diameter. The size of the molecule will not affect its chances of escape, for each hole is about ten thousand times as wide as a molecule. The chance

of a molecule going through any particular hole is proportional to its chance of hitting it. If a molecule travels at twice the speed of another it will hit the side of the vessel twice as often and have twice the chance of finding the hole. The number of molecules of any one kind passing through the hole is proportional to their chance of hitting it, *i.e.*, to their velocity. Accordingly, if $r$ is the rate of diffusion $v = kr$. We have seen that $\frac{d_1}{d_2} = \frac{{v_2}^2}{{v_1}^2}$

and so $$\frac{d_1}{d_2} = \frac{(kr_2)^2}{(kr_1)^2}$$

$$\therefore \quad \frac{d_1}{d_2} = \frac{{r_2}^2}{{r_1}^2},$$

which is Graham's law of diffusion.

The phenomenon may be illustrated by a well-known experiment. A porous pot is connected with a ∪-tube containing a coloured liquid as indicator and is surrounded first with a beaker of carbon dioxide, which is heavier than air, then with a beaker of hydrogen, which is lighter than air. In the first case the lighter air diffuses out of the pot quicker than the heavier carbon dioxide diffuses in, and the reduction of pressure is shown by the motion of the liquid. In the second case (B) the hydrogen diffuses into the pot quicker than the air diffuses out and the pressure in the pot is raised.

**54. Applications of Graham's Law.**—Two practical uses of this

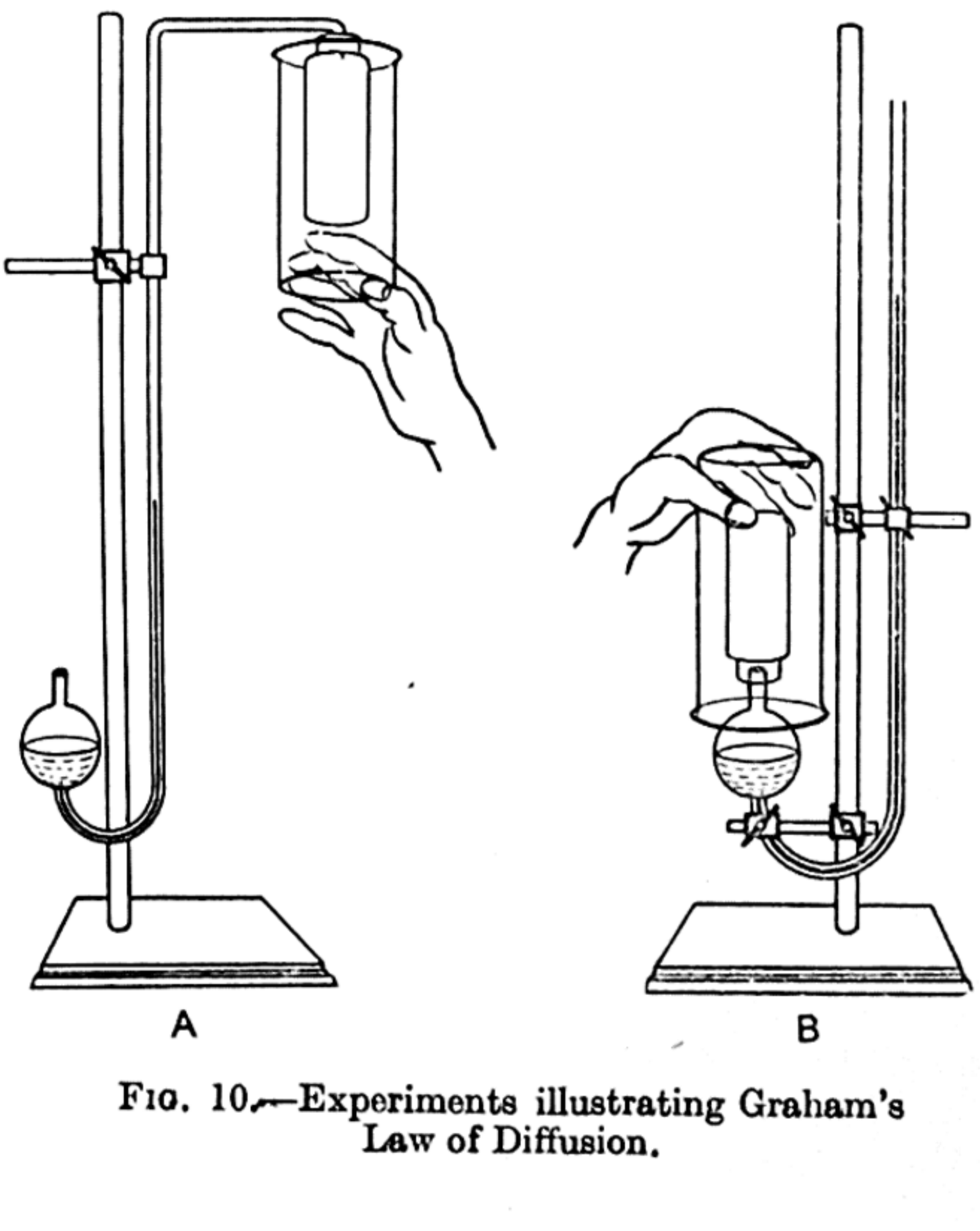



FIG. 10.—Experiments illustrating Graham's Law of Diffusion.

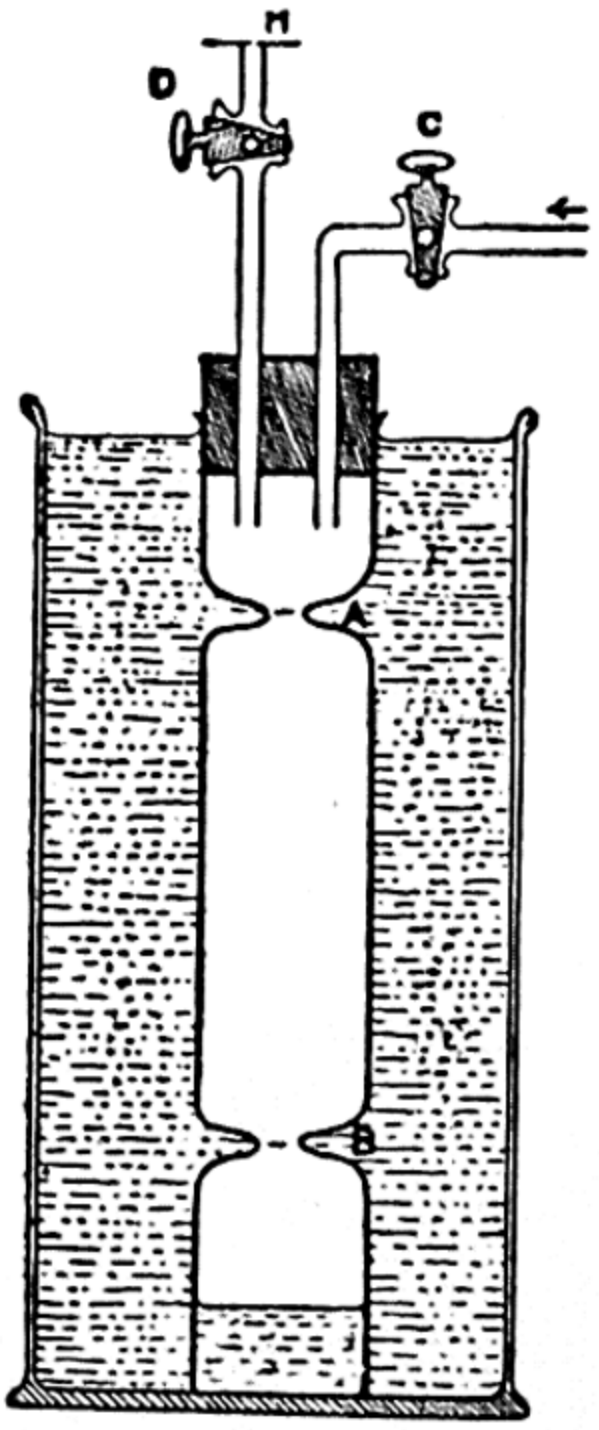



FIG. 11.—Determination of the density of a gas by its rate of effusion.

law have been made: (1) For the separation of mixed gases. (2) For the determination of the density of gases.

(1) If a mixture of two gases of different densities is passed through a porous tube, the lighter gas will pass through more quickly than the heavier. Thus, if a mixture of hydrogen and oxygen (as obtained by the electrolysis of water) be allowed to pass through a long clay pipe stem and is then collected over water the resultant gas will contain so little hydrogen that it will not explode.

The method has been applied to the separation of the isotopes (§ 148) of neon, which have densities 10 and 11 respectively. Their rates of diffusion are then as $\frac{1}{\sqrt{10}} : \frac{1}{\sqrt{11}}$, *i.e.* 1 : 0·953. This very small difference makes it necessary to perform many diffusions before obtaining any measurable separation, but in spite of these difficulties a measurable degree of separation has been obtained.

**55. Determination of the Relative Density of a Gas from its Rate of Effusion.**—The relative density of a gas may be determined by measurement of the rate of diffusion, but the analogous rate of *effusion* is more often employed. Graham's law applies equally to the rates of diffusion and effusion, which is the rate at which a gas, when impelled by pressure, escapes through a minute aperture. The apparatus shown in Fig. 11 is often employed.

A wide tube has two constrictions (A, B) marked with lines. The top of the tube has fitted to it two tubes and stopcocks, through one of which gas can be forced into the tube while the other communicates with a piece of platinum foil pierced with a minute hole, H. The tube is filled with air, of which the density is known. The stopcock, C, is closed and D opened, and the time ($t_1$) needed for the escape of the gas from the part of the tube between the constrictions B and A is noted. The air is then completely replaced by the gas to be measured, and the time ($t_2$) needed for the same volume of gas to escape is noted. The rate of effusion is the volume escaping divided by the time. Thus, using the formula obtained ($d_1$, $t_1$ are the density and time of escape for air, $d_2$, $t_2$ for the gas to be measured),

$$\frac{d_1}{d_2} = \frac{\left(\frac{v}{t_2}\right)^2}{\left(\frac{v}{t_1}\right)^2}$$

$$\frac{d_1}{d_2} = \frac{{t_1}^2}{{t_2}^2}$$

$$d_2 = \frac{d_1 {t_2}^2}{{t_1}^2}$$

Thus, if the air (density 14·4) escaped in 152 seconds and the gas in 219 seconds the density of the latter is given by

$$d = \frac{14{\cdot}4 \times 219^2}{152^2}$$
$$= 29{\cdot}9.$$

The molecular weight of the gas would be twice this value, *i.e.*, 59·8.

## Molecular Weights of Substances in Solution

**56. The Nature and Measurement of Osmotic Pressure.**—It has been found that certain substances, such as the membranes of animals and plants, allow water to pass through them but do not allow other substances dissolved in the water to do so. Membranes of this kind are said to be *semipermeable*. Now it is found that if two solutions of the same substance but of different strength are separated by a semipermeable membrane *they tend to equalise their strengths* by the passage of the solvent through the membrane.

The pressure which must be exerted upon the solution to prevent the solvent from travelling through the membrane is called *osmotic pressure* and the passage of the solvent is called *osmosis*. The process may be easily demonstrated as follows: A piece of pig's bladder is tied over the end of a thistle funnel and the joint made thoroughly water-tight with marine glue. The globe of the funnel is filled with sugar solution (A) and it is immersed in water (B). We have here a strong solution and an infinitely weak solution separated by a semipermeable membrane. The process of *osmosis* will tend to equalise the strengths of these solutions and the *osmotic pressure* of the solution A acting in all directions increases its volume, and water flows in through the membrane. The liquid rises in the tube until the hydrostatic pressure of the solution, acting downward, is equal to the osmotic pressure, acting upward. If this apparatus could be made quite free from leakage the osmotic pressure of sugar solution could be determined in gm./cm.$^2$ by measuring the height (CD) of the column of the liquid, and multiplying it by the density of the sugar solution.

Animal membranes are always very prone to leakage, but Pfeffer (1877)

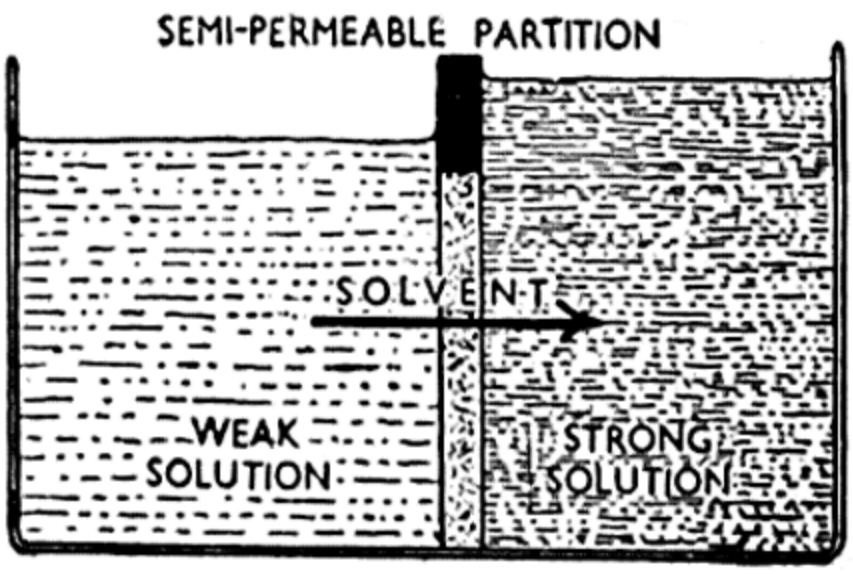



Fig. 12.—Movement due to Osmotic Pressure.

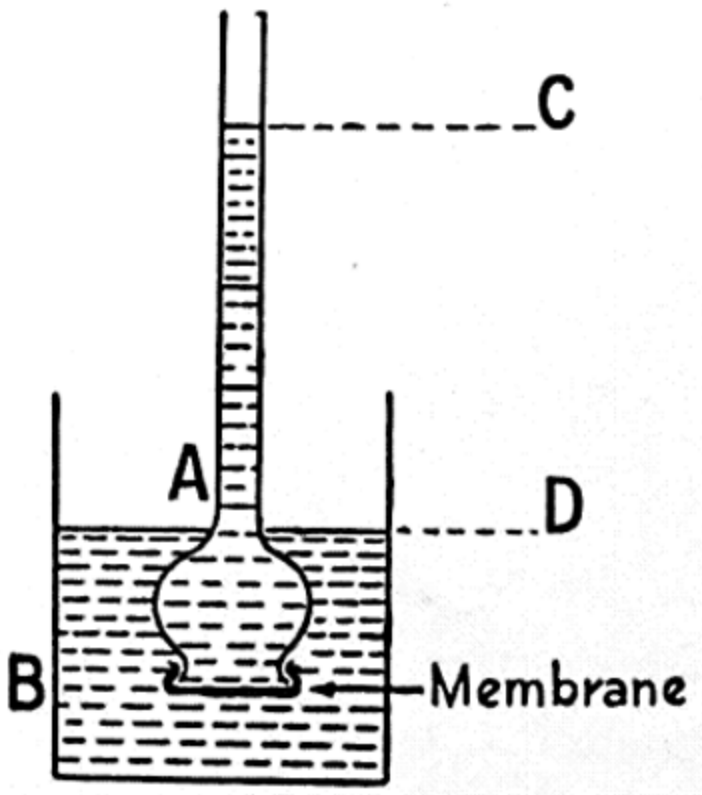



Fig. 13.—Osmosis.

constructed a new type of membrane by depositing copper ferrocyanide in the pores of a porous pot. The pot is carefully freed from air, filled with dilute copper sulphate solution and immersed in potassium ferrocyanide solution. These meet in the interstices of the pot and there precipitate the slimy colloidal copper ferrocyanide. This forms an admirable semipermeable membrane and it is so well supported by the fabric of the pot that it will stand a pressure of several atmospheres. The prepared porous pot is fitted by a strong adapter to a manometer which measures the pressures produced. In this way osmotic pressures have been measured with considerable accuracy.

When Pfeffer measured the osmotic pressures of various solutions he found the remarkable fact that, *if a given weight of a substance be dissolved to form a given volume, v, of solution, the osmotic pressure of this solution will be the same as the gas pressure which would be exerted by the same weight, w, of the substance in the form of gas confined in a space of volume, v, both measurements being made at the same temperature.*

Thus, for example, Pfeffer found that a 1 per cent. cane-sugar solution had an osmotic pressure of 505 mm. of mercury at 6·8° C.

Imagine the same weight of cane-sugar (1 gm.) in the form of a gas occupying 100 c.c. volume at 6·8° C. If cane-sugar were a gas the gram-molecular weight, 342 gms., would occupy 22·4 litres at 760 mm. pressure at 0° C.

And 342 gms. would occupy $22{\cdot}4 \times \frac{279{\cdot}8}{273}$ l. at 6·8° C. and 760 mm. pressure.

1 gm. would occupy this volume at $\frac{760}{342}$ mm. pressure.

1 gm. would occupy 100 c.c. at $\frac{760 \times 22{\cdot}4 \times 279{\cdot}8}{342 \times{\cdot}1 \times 273} = 510$ mm.

In view of the difficulty of accurate osmotic pressure determinations the agreement between the experimental value, 505 mm. and the calculated value, 510 mm. is very close.

The basic fact of osmosis is that a solute cannot pass through a semipermeable membrane whilst a solvent can. Hence the number of solvent molecule bombardments on the solution side of the membrane is smaller than on the solvent side, and more solvent molecules pass into the solution than out of it. Pressure has to be applied to the solution to stop the differential flow, and this is the osmotic pressure. The total number of bombardments on both sides of the membrane is the same, but, in the diagram, nine solvent molecules pass into the solution for every six that pass out. Hence the differential flow of solvent into the solution.

If it is asked why a solution of salt with an osmotic pressure of 50 atmospheres does not burst the fragile glass bottle in which is is kept, it should be realised that the pressure is tending to increase the volume of the liquid and can only be exerted within the liquid. The tendency of the liquid to increase in volume is balanced by a corresponding strain existing in the liquid and can only manifest itself if some means is provided, *e.g.*, a semipermeable membrane, by which solvent can enter and the volume of the liquid increase.

This *bombardment* theory of osmotic pressure is not everywhere accepted. The "vapour sieve" theory of Callendar has much to recommend it. In this theory it is supposed that the semipermeable membrane contains minute pores through which the vapour of the solvent can pass. The vapour pressure of the solution is lower than that of the solvent at the same temperature,

and consequently the solvent evaporates from the weaker solution and condenses in the stronger until the concentrations of both are the same. For a discussion of the merits of these theories, a work on Physical Chemistry should be consulted.

**57. Osmotic Pressure and Molecular Weights.**—The significance of this discovery is that it affords a method of finding the molecular weight of a substance which cannot be volatilised. If we know that a solution containing a weight $w$ gms. of a substance dissolved so as to form $v$ c.c. of solution at $t°$ C. has an osmotic pressure of $p$ atmospheres ; then $w$ gms. of the substance at a temperature $t°$ and pressure $p$ atm. would have a volume of $v$ c.c. if it could be obtained in the form of a gas, and we can calculate the molecular weight by the usual methods (§ 51).

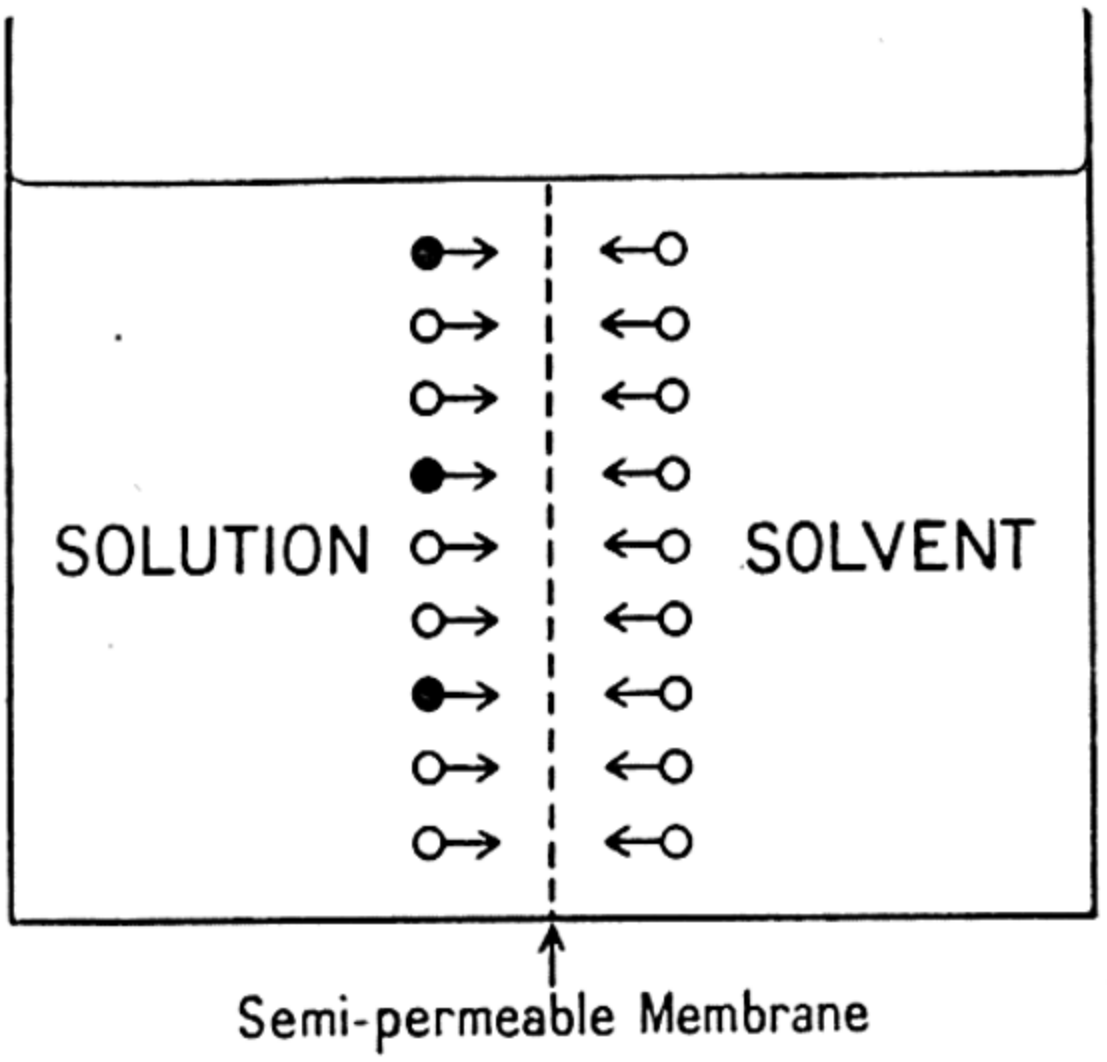



FIG. 13A.

Let us suppose that a 0·2 per cent. solution of a solid has an osmotic pressure of 55 cm. of mercury at 20° C. ; and that we wish to find its molecular weight.

0·2 gm. of solid in 100 c.c. solution at 20° C. has an osmotic pressure of 55 cm. of mercury.

Then 0·2 gm. of the substance as a gas at 20° C. at a pressure of 55 cm. mercury would have a volume of 100 c.c.

And 0·2 gm. at 0° C. and 76 cm./Hg pressure would have a volume of $100 \times \frac{273}{293} \times \frac{55}{76}$ c.c.

$\therefore$ 22·4 litres would be the volume of $\frac{0{\cdot}2 \times 22{,}400 \times 293 \times 76}{100 \times 273 \times 55}$ gms.

Molecular weight = 66·4 approx.

The method is rarely used owing to the superior accuracy and simplicity of the methods which follow, but is of great theoretical interest.

**58. Osmotic Pressure and Vapour Pressure.**—It may be shown that there is a necessary connection between the *osmotic pressure* of a solution and

its *vapour pressure*. It is not thought necessary to give the proof here, but the conclusion reached theoretically and confirmed by experiment is that *the difference between the vapour pressure of the pure solvent and the vapour pressure of a dilute solution is proportional to the osmotic pressure of the solution in question*. The osmotic pressure of a solution of a given strength is inversely proportional to the molecular weight and, accordingly, *the lowering of vapour pressure resulting from the addition of a given weight of solute to a given volume of solvent is inversely proportional to the molecular weight of the solute*.

Now two easily measurable quantities, the boiling point and the freezing point, depend upon the vapour pressure. The boiling point of a solution is the temperature at which the vapour pressure of the solution in question becomes equal to the vapour pressure of the atmosphere; and the freezing point of an aqueous solution is the point at which the vapour pressure of the solid solvent and the solution are the same. It can be proved both theoretically and by experiment that the lowering of the freezing point and the raising of the boiling point of a solution of given strength are inversely proportional to the molecular weight of the solute.

If we express this mathematically we may say that if a solution of given concentration boils or freezes at $t^1$° C. while the pure solvent boils or freezes at $t$° C. $(t \sim t^1) \propto \frac{1}{M}$ for a solution of given concentration and $t \sim t^1 = \frac{k}{M}$.

Extending this to a solution of any concentration, say $w$ gms. per S c.c.

We have $$t - t^1 = \frac{cw}{MS}$$

where $c$ is a constant depending upon the units employed, and the latent heat of fusion or vaporisation of the solvent.

If $c$ is determined by experiment (or theoretically), M, the molecular weight of a dissolved substance is readily determined by measuring the change in the boiling or freezing point $(t \sim t^1)$ when $w$ gms. of the substance are added to 100 c.c. of solvent.

**59. Boiling Point or Ebullioscopic Method.**—The accurate measurement of a boiling point accurate to 0·01° C. or less is difficult owing to the tendency of the liquid to superheat. Several methods have been devised, of which that of Beckmann (Fig. 14) is the easiest to understand, if not to use. A weighed amount of the solvent (S gms.) is placed in the inner tube, which contains pieces of porous pot, to ensure regular boiling and thorough mixing of liquid and vapour. A water-cooled tube condenses the vapour and returns the liquid to the central tube. The boiling point ($t$) is measured by a Beckmann thermometer graduated over a range of 6° C. in hundredths of a degree. The mercury is adjustable to allow of any range of 6° C. being covered. A weighed pellet of the solid ($w$ gms.) is then added through the side tube and the boiling point ($t^1$) again read. From the formula established above

$$t^1 - t = \frac{cw}{SM}$$

where $c$ is a constant (520 for water) and M is the molecular weight of the solid added.

**60. Freezing Point or Cryoscopic Method.**—The apparatus is shown in Fig. 15.

S gms. of the solvent are weighed into the inner tube and in this is placed the Beckmann thermometer. The tube is enclosed in an air jacket, which

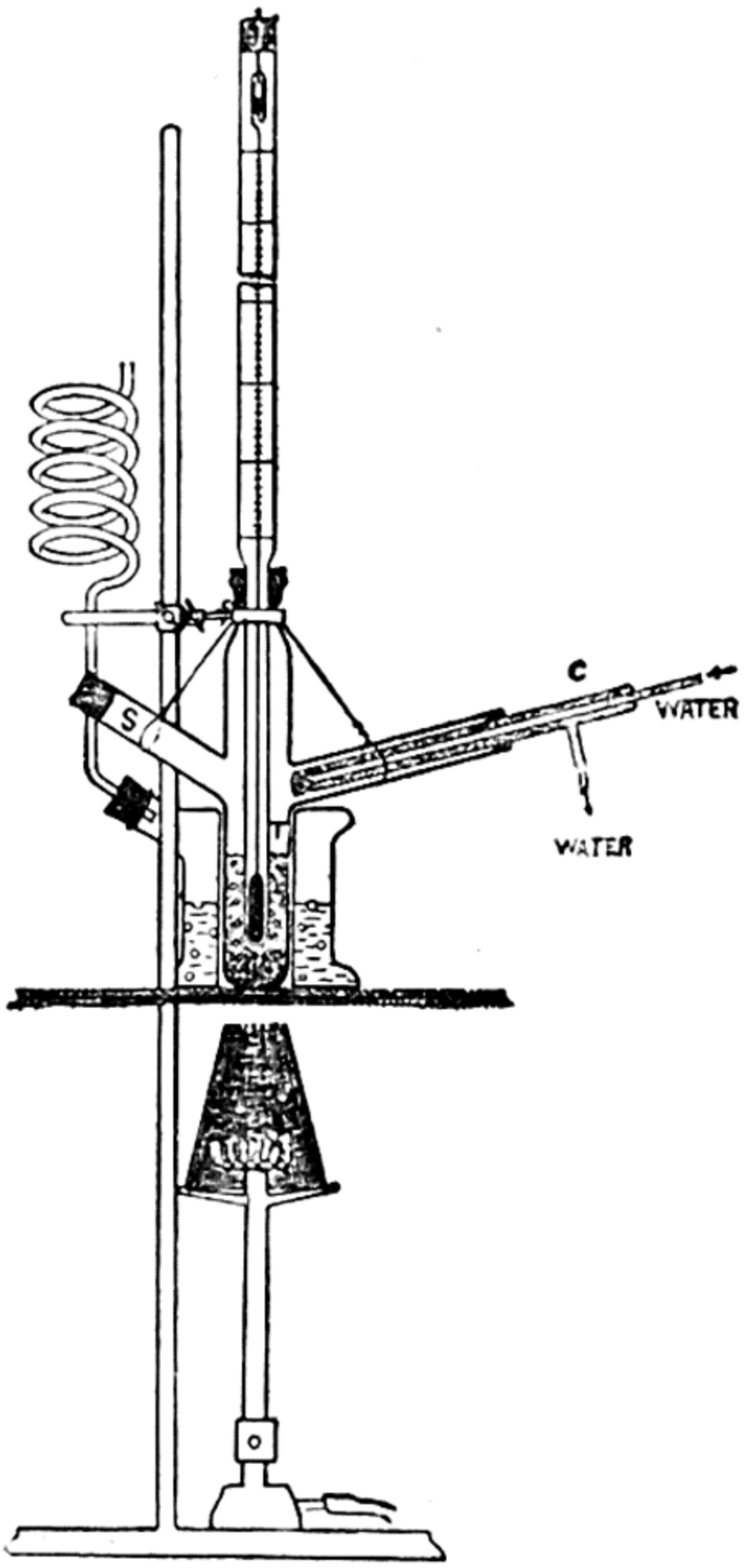



FIG. 14.—Determination of Molecular Weight by the Ebullioscopic Method.

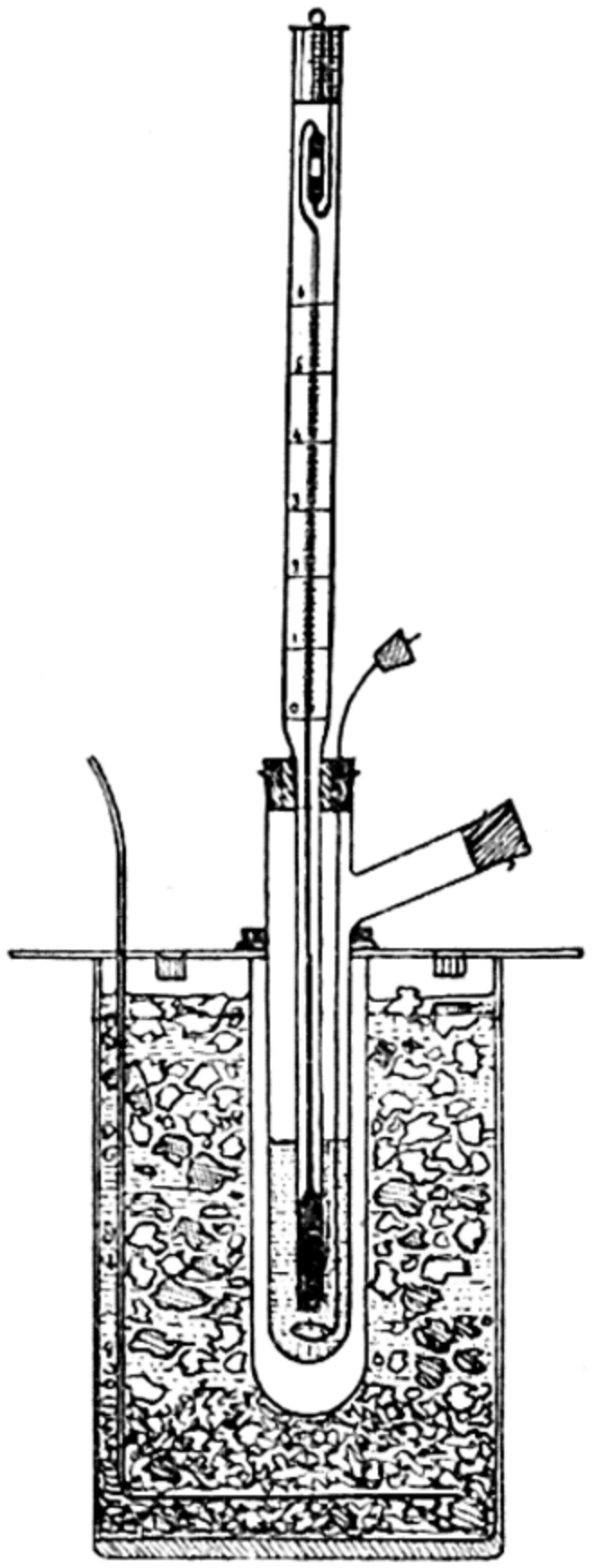


FIG. 15.—Determination of Molecular Weight by the Cryoscopic Method.

is surrounded by a freezing mixture. The solvent is stirred steadily by means of the stirrer, and the mercury thread watched. This falls until a point a little below the true freezing point is reached, when freezing occurs. It then rises and remains steady at the freezing point $t$. A pellet of solute, weight $w$ gms., is dissolved in the solvent by removing the inner tube, warming it, and stirring. The new freezing point ($t^1$) is then determined in the same way as before. Then $t - t^1 = \frac{cw}{SM}$ as before, $c$ in this case being 1,850 for water.

*Cryoscopic and Ebullioscopic Constants for Some Solvents*

If $t$ is the change of boiling or freezing point of S gms. of a solvent when $w$ gms. of solute of molecular weight M are dissolved in it, then $t = \frac{cw}{SM}$ if $c$ has the value given below.

## ATOMIC WEIGHTS.

**61. Atomic Weights, Combining Weights and Valency.**—We have seen in Chapter II. how the *equivalent* or *combining weight* of an

| Solvent. | Cryoscopic constant ($c$). | Ebullioscopic constant ($e$). |
|---|---|---|
| Water . . . | 1,850 | 520 |
| Acetic acid . . | 3,900 | 3,070 |
| Benzene . . . | 5,000 | 2,560 |
| Phenol . . . | 7,300 | 3,600 |
| Chloroform . . | — | 3,880 |
| Acetone . . . | — | 1,670 |

element is determined. We may now survey the methods by which we can determine the atomic weight.

Let us suppose that an element (A) forms with hydrogen a compound the formula of which we do not know. Evidence such as that detailed in § 48 makes it likely that one hydrogen atom never combines directly with more than one atom of any other kind.[1] The formula of our hydrogen compound may then be AH, $AH_2$, $AH_3$, $AH_4$, etc.

Now the equivalent weight of A is the weight of it which combines with 1 part by weight of hydrogen. It follows then that if we call the weight of a hydrogen atom 1, and the weight of an A atom expressed in the same unit $a$, then the equivalent (the weight of A combined with 1 part by weight of hydrogen) will be $a$ if the formula of its hydrogen compound is AH, $\frac{a}{2}$ if the formula is $AH_2$, $\frac{a}{v}$ when the formula is $AH_v$.

Now the number of hydrogen atoms with which an atom of an element combines is called the valency ($v$), and the weight $a$ of an atom of A, expressed in terms of the weight of an atom of hydrogen, is called the atomic weight of the element.

We see then that if the valency of an element is $v$ and its atomic weight is $a$, its combining weight is $\frac{a}{v}$.

We assume and are confirmed by experiment in thinking that one hydrogen atom never combines with more than one atom of another element. From the definition of valency and the fact that atoms are indivisible we may deduce that the valency of an element is a small whole number. We have then

$$\frac{\textit{Atomic weight}}{\textit{Combining weight}} = \textit{a small whole number.}$$

or **atomic weight = combining weight × a small whole number.**

[1] Hydrazoic acid, $HN_3$, is no exception since its formula is $H - N = N \rightleftharpoons N$, but exception might be found in the hydrogen bond.

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The importance of this result lies in the fact that the combining weight can be determined with great exactness by analytical methods, while the methods which give the atomic weight directly give only an approximate result. But if an *approximate* value is obtained for the atomic weight, this will be enough to indicate the small whole number by which the combining weight must be multiplied to give the *exact* result. Thus the combining weight of an element might be found to be exactly 9·01. Approximate values for the atomic weight obtained by, say, Dulong and Petit's law (§ 63) might give a figure of 28. We then have

$$28 \text{ (approx.)} = 9{\cdot}01 \times \text{a small whole number.}$$

The small whole number (*i.e.*, the valency) must then be 3 and the *exact* atomic weight $3 \times 9{\cdot}01 = 27{\cdot}03$.

The practical methods available for getting a more or less approximate value for the atomic weight include :—

(1) The consideration of the molecular weights and composition of a number of volatile (or soluble) compounds of the element.

(2) Dulong and Petit's law.

(3) Evidence drawn from the periodic table and X-ray spectra.

(4) The use of the mass spectrograph.

The first three are discussed in this chapter. The last is described in Chapter VII.

**62. Molecular Weights and Atomic Weights.**—(1) The molecular weights of volatile compounds of an element are readily determined by the methods of §§ 51–55.

The percentages of the various elements contained in these volatile compounds can be obtained by methods which do not require any assumption to be made as to the atomic weights of these elements.

Suppose a compound of elements A and B exists. Its formula is, of course, unknown since formulæ cannot be determined without a knowledge of atomic weights. So let this formula be represented as $A_nB_m$. If $a$ is the atomic weight of element A, and $b$ the atomic weight of element B, the gram-molecular weight of the compound is $na + mb$ grams. We can find the gram-molecular weight by experiment; let it be M.

Then $$na + mb = \text{M}.$$

Let us now analyse the compound and assume that we find it contains $x$ per cent. of the element A.

Then the gram-molecular weight of the compound contains $\frac{\text{M} \times x}{100}$ gms. of the element A. But the gram-molecular weight contains $na$ gms. of this element.

Then $$\frac{Mx}{100} = na$$

and since M and $x$ can be found by experiment a value for $na$ is obtained. Now $n$ is the number of atoms in a compound and must be a whole number and cannot be less than one.

If then we determine the molecular weight and composition of a number of different volatile compounds of the same element we shall find a number of different values for $na$. These will all be multiples of $a$, and the least value obtained for $na$ will probably be $a$, when $n$ is one and there is only one atom of the element A in the compound. In this way **the least weight of an element contained in one molecular weight of any compound is probably the atomic weight.**

Since the simplest compounds are the most volatile and so best adapted to molecular weight determinations it is very unlikely that we should not find one at least of these which contains only one atom of the element in its molecule ; none the less, the possibility of such an error must not be neglected.

As an example we may take the determination of the atomic weight of carbon. If we convert carbon into carbon dioxide we find that 3 gms. of the former produce 11 gms. of the latter. Thus 8 gms. of oxygen combine with 3·00 gms. of carbon, and the combining weight of carbon is therefore 3·00. The percentage of carbon in the volatile compounds mentioned in the table below may be in every case determined by converting a known weight of them into carbon dioxide, 3/11 of which by weight we know to be composed of carbon.

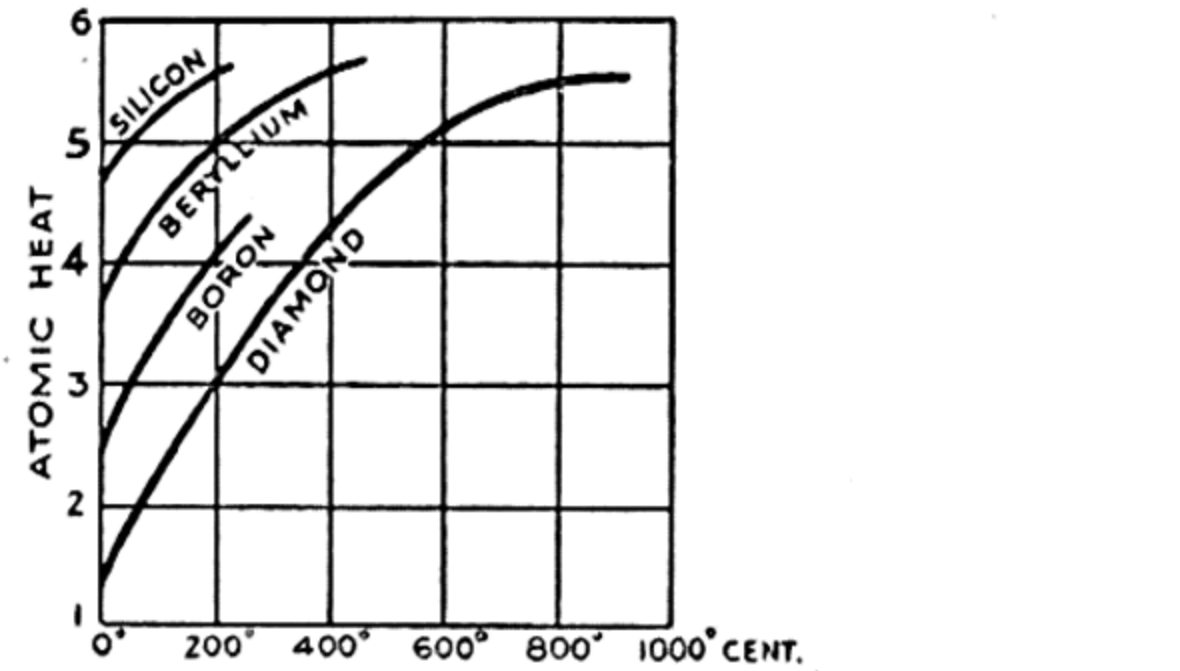
The last column contains values which are all multiples of 12 and

| Compounds. | M Molecular Weight (from Vapour Density). | $x$ Percentage of Carbon in the Compound. | $na$ Weight of Carbon in one gm.-molecule. |
|---|---|---|---|
| Carbon monoxide . | 28 | 42·9 | 12 |
| Carbon dioxide . . | 44 | 27·27 | 12 |
| Methane . . . | 16 | 75·0 | 12 |
| Ethylene . . . | 28 | 85·7 | 24 |
| Benzene . . . | 78 | 92·3 | 72 |

the least value is 12 itself ; so we assume that the first three compounds contain only one atom of carbon, and therefore conclude that the atomic weight is 12. The combining weight of carbon is 3·00, and so the atomic weight is $4 \times 3{\cdot}00 = 12{\cdot}00$, and the valency is 4.

This method is applicable to almost all elements, for even the metals form a good many volatile organic compounds. It is not, however, so easily applied to new elements obtainable only in very minute quantities, owing to the difficulty of determining vapour densities when only minute amounts of material are available.

**63. Dulong and Petit's Law.**—Dulong and Petit, as long ago as 1819, put forward the theory which, expressed in modern form, states



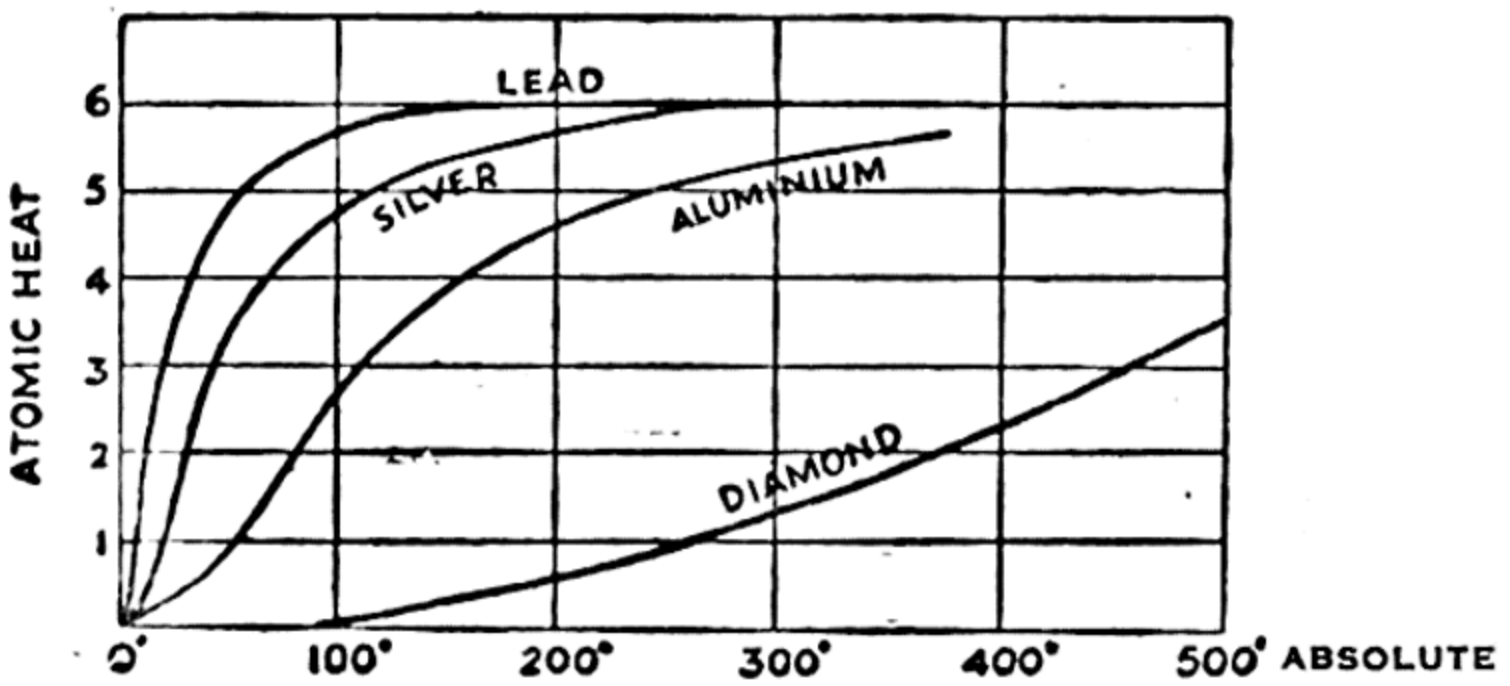




FIG. 16.—Variation of Atomic Heat with Temperature.

that *the product of the atomic weight* (*a*) *and the specific heat* (*s*) *of a solid element is approximately equal to* 6·4. This law holds for the great majority of elements, but notable exceptions are presented by carbon, boron, silicon, solid oxygen and hydrogen, and to a less extent sulphur and phosphorus. The value *as*, known as the atomic heat, is in fact not constant, and varies with the temperature. The specific heats of the elements approach zero as the absolute zero of temperature is approached. The atomic heat falls with temperature at first slowly, then rapidly, then slowly again.

The curve for the variation of atomic heat with temperature in the case of most elements cuts the temperature range 0°–100° C., between which temperatures specific heats are usually determined, in its comparatively flat portion (Fig. 16), which lies between the atomic heat values 6·0–6·5. A few elements, however, are exceptional and, although their atomic heats do ultimately reach a value

near the latter figure, they do not do so until very high temperatures are reached. Dulong and Petit's law is, however, a useful guide if its limitations are remembered.

As an example we may take a determination of the atomic weight of copper.

The equivalent of copper is 31·8 and its specific heat at 0° C. is 0·09. Then

$$\text{atomic weight} \times \text{specific heat} = 6{\cdot}4 \text{ (approx.)}$$

$$\text{atomic weight} = \frac{6{\cdot}4}{{\cdot}09}$$

$$= 71{\cdot}1 \text{ (approx.)}$$

$$\therefore 31{\cdot}8 \times \text{valency} = 71{\cdot}1 \text{ (approx.)}$$

$$\therefore 31{\cdot}8 \times 2 = \text{atomic weight}$$

$$\therefore \text{atomic weight} = 63{\cdot}6.$$

In the example taken the specific heat of copper at 100° C. would have given a better value, but with a new element one has no guide as to the best temperature at which to determine the specific heat. Even with the value taken it is quite clear that $2 \times 31{\cdot}8$ $(= 63{\cdot}6)$ is much nearer 71·1 than is $1 \times 31{\cdot}8$ or $3 \times 31{\cdot}8$, and this is all we need to know.

**64. The Periodic Law.** (See Chapter VII. for further details).—If the elements are tabulated according to atomic weight and chemical properties by the system of Mendeléeff, any new element[1] must have an atomic weight, which will enable it to fit into a vacant space. Its chemical properties will help to indicate the space to which it belongs, and, this space once decided on, an approximate atomic weight is obtained, for its atomic weight must then lie between the values of the right-hand and left-hand neighbouring elements, or at any rate must not differ from them by more than one or two units.[2]

Thus, suppose the element tin to be newly discovered. One of its equivalents is 29·75, and its atomic weight may therefore be 29·75, $2 \times 29{\cdot}75$, $3 \times 29{\cdot}75$, $4 \times 29{\cdot}75$, $5 \times 29{\cdot}75$, etc. Its general likeness to lead would indicate a position in Group IV. and on looking at the periodic table we should find that the position in the Table indicated for atomic weight 29·75 corresponds to no vacant space but is between silicon and phosphorus, typical Group IV. and Group V. elements. The value, 59·5, $(2 \times 29{\cdot}75)$ brings us into the iron, cobalt, nickel space. Tin has no particular resemblance to these elements and there is no room for it unless we suppose the first transition period to be longer than the second. The value 89·25,

[1] That is to say, any element with new chemical properties, not merely an *isotope* of an element already known (see Ch. VII.).

[2] Cf. cases of argon and potassium, iodine and tellurium (§§ 1249, 968).

(3 × 29·75) would place tin between strontium and yttrium in a place where the periodic table has no space. The value 119·0, (4 × 29·75) finds a space ready for an element with likenesses to lead and germanium, which tin undoubtedly possesses. The value, 5 × 29·75 = 148·75, would make tin a 'rare-earth' element[1] and 6 × 29·75 = 178·5 would give a space which is occupied by hafnium and would in any event require an element of Group IVa., like zirconium or thorium, with which the valency of 6 which we have assumed would be incompatible. 7 × 29·75 = 208·25 would find an empty space, but one which should be occupied by a halogen, which might have a valency of 7 and some metallic character, but which would hardly resemble tin. An element with atomic weight 8 × 29·75 = 236 would almost certainly be radio-active, which tin is not, and also would not have the valency 8 which we are assuming, but probably that of 5, lying, as it would, between uranium and thorium. Consequently we find the only suitable space for our "new element" indicates a valency of 4 and an atomic weight of 119·0.

The position of an element in the periodic table may now be directly determined from measurements of its X-ray spectrum. The position in the periodic table gives the atomic weight within a few units, and from this approximate value the valency and the exact atomic weight can be obtained.

**65. Physical Methods of Determining Atomic Weights.**—*Limiting Density Method.*—If the molecular weight of a gas could be determined with as great an accuracy as the chemical equivalent of an element, it would afford an excellent method of determining atomic weights. Thus if we know that the molecular weight of nitrogen is 28·016 and, by the methods of § 62, that its atomic weight is approximately 14, its exact atomic weight must be 14·008. Again if the precise molecular weight of phosphine is 33·930 and the equivalent of phosphorus is nearly 10·3 we can deduce that its formula is $PH_3$ and that the precise atomic weight of phosphorus is $33{\cdot}930 - 3 \times 1{\cdot}008 = 30{\cdot}906$. Very accurate determinations of the density of permanent gases can be made, but the assumption that the molecular weight is twice the density of a gas relative to oxygen = 16 is only precisely true for perfect gases, *i.e.*, for those which obey Boyle's law exactly. No actual gas fulfils these conditions, but as their pressure is made lower, so they more and more nearly conform to it. So in practice (1) accurate density determinations are made, (2) the extent to which the gases deviate from Boyle's law is experimentally determined, (3) the density of the gas at very low pressure relative to oxygen (= 16) at very low pressure is worked out, and twice this value gives the precise molecular weight, from which the atomic weight can be deduced as above.

*Other Methods.*—The measurement of positive-ray parabolas (§ 148) gives us the atomic weight of an element with fair accuracy.

The mass-spectrograph, as devised by Aston and perfected by him and other workers, affords a method of determining atomic weights with accuracy equal to, or surpassing that of the best chemical methods.

[1] Incompatible with a character or valency of 5.

The importance of this method is rapidly increasing; it is further and more fully discussed in § 149. Its merits are its high accuracy, the small quantity of material needed and the possibility of using imperfectly purified material.

**66. Atomic Weight and the Formulæ of Compounds.**—The process of finding the atomic weight of an element consists then, first of finding an approximate value for the atomic weight ($w$) by the methods just detailed. The equivalent ($e$) of the element is then determined and the valency is found from the relation.

$$ev = w.$$

The valency being known we obtain the formulæ of the simpler compounds. Thus, in the case of bismuth the equivalent found, say, by converting the metal into its oxide is found to be 69·7. The atomic weight, as determined by the methods of §§ 62–65, appears to be about 207

$$\therefore\ 69{\cdot}7 \times \text{valency} = \text{about } 207$$
$$\therefore\ \text{valency} = 3.$$

Bismuth chloride is therefore $BiCl_3$, the oxide $Bi_2O_3$, etc.

**67. Standards of Atomic Weight.**—It is, of course, necessary to have a standard of atomic weight. The absolute weight of an atom in grams is less than $10^{-20}$ gms., and is not known with the same degree of exactness as are the *relative* weights of different kinds of atoms.

Hydrogen was selected by Dalton as the standard of equivalent and atomic weights, and for many years was retained as such, its atomic weight and equivalent weight being taken as unity, 1·000.

There is, however, a serious defect in this system. The most accurate methods of determining equivalents do not, as a rule, involve compounds of hydrogen, and metals do not form any stable hydrogen compounds. The equivalents of most elements are determined from the composition of their oxides or chlorides, and one of these elements is therefore a better standard. If we take hydrogen as standard our determination of an equivalent by means of the formation of an oxide (p. 39) depends on :

(1) The knowledge of the equivalent of oxygen.

(2) The determination of the equivalent of the metal in terms of the equivalent of oxygen.

Thus if it was found that any small error existed in (1) it would affect the majority of atomic weights.

Moreover, hydrogen is an element rather exceptional in its atomic structure, and, if we take it as standard, fewer elements have atomic weights approximating to whole numbers than if we take the value oxygen = 16·000.

Accordingly, oxygen has been taken as of atomic weight 16·000, and of equivalent 8·000.

Even this standard now requires further definition. Chemical determinations take the weight of the average oxygen atom, including $O^{16}$, $O^{17}$, $O^{18}$, as 16·0000; determinations based on the mass-spectrograph take the mass of the $O^{16}$ atom as 16·0000. The difference resulting is about one part in a hundred thousand. The proportions of the various oxygen isotopes are constant in any given specimen of the gas, but the proportions of $H^1$ and $H^2$ in hydrogen vary with its mode of preparation. This affords an additional reason for taking oxygen rather than hydrogen as the standard in atomic weight determinations.

**68. Practical Determination of Atomic Weights.**—The determination of an atomic weight is a process which can attain great accuracy. The method adopted to find the exact atomic weight of an element of which the approximate atomic weight and the valency have already been found usually consists of one of the following :—

(1) A weighed quantity of the element is made to combine with an element of known atomic weight to form a compound of known formula, and the weight of this compound formed is ascertained.

Thus, suppose it is found in a certain experiment that 3·4602 gms. of a certain trivalent metal X are converted into 4·4031 gms. of the oxide $X_2O_3$.

Then $$2X + 3O = X_2O_3,$$

and if the atomic weight of the metal X be $x$, $2x$ gms. of metal form $2x + 3 \times 16{\cdot}000$ gms. oxide.

But 3·4602 gms. of metal form 4·4031 gms. oxide.

$$\therefore \quad \frac{2x + 48}{2x} = \frac{4{\cdot}4031}{3{\cdot}4602}$$

$$\therefore \quad 2x\,(4{\cdot}4031 - 3{\cdot}4602) = 48 \times 3{\cdot}4602$$

$$x = \frac{48 \times 3{\cdot}4602}{0{\cdot}9429}$$

$$= 176{\cdot}1.$$

(2) The most usual method is to convert a known weight of a compound of the element into another compound and find the weight of this product.

Thus, let us suppose that 4·0231 gms. of the oxide of a divalent element X can be converted into 8·6361 gms. of the sulphate.

$$XO + H_2SO_4 = XSO_4 + H_2O.$$

The atomic weight of the element X may be called $x$, that of sulphur is very accurately known as 32·06, while that of oxygen is standard 16·000.

Then the molecular weight of XO is $x + 16{\cdot}000$, and the molecular weight of $XSO_4$ is $x + 32{\cdot}04 + 4 \times 16{\cdot}000$.

$$\therefore \quad \frac{x + 16}{x + 96{\cdot}06} = \frac{4{\cdot}0231}{8{\cdot}6361}$$

$$x\,(8{\cdot}6361 - 4{\cdot}0231) = 96{\cdot}06 \times 4{\cdot}0231 - 16 \times 8{\cdot}6361$$

$$x = \frac{386{\cdot}4590 - 138{\cdot}1776}{4{\cdot}6130}$$

Atomic weight of X = 53·82.

The last-mentioned method is in theory less reliable than the first, for it necessarily involves the use of other atomic weights beside that of the standard oxygen. None the less, it is the most important method, and it is therefore very necessary that the atomic weights of certain common elements should be known with great accuracy in order to aid in the determination of the remainder. Those chiefly required are the atomic weights of hydrogen, chlorine, silver, nitrogen and sulphur.

These are known, for reasons to be discussed later, to be approximately 1, 35·5, 108, 14 and 32 respectively. The problem is rather how to determine them as exactly as possible.

**69. The Atomic Weight of Hydrogen.**—*Preliminary.*—Hydrogen has the formula $H_2$, as follows from the arguments of § 48. When two parts of hydrogen by volume combine with one part of oxygen by volume, two parts of steam by volume are formed (v. also § 196). It follows then that two molecules of hydrogen combine with one molecule of oxygen to form two molecules of steam. The molecule of oxygen contains at least two atoms, for it must contribute at least one atom to each molecule of steam. That it does not contain more than two atoms we conclude from the fact that in no chemical reaction does one volume of oxygen produce more than two volumes of a gaseous oxide (*cf* § 48); and also from its physical properties (ratio of specific heats at constant volume and constant pressure). We may then say that the formula of water must be $H_2O$.

$$2H_2 + O_2 = 2H_2O.$$

Let the atomic weight of hydrogen be $x$. The atomic weight of oxygen is 16 (standard). Then in a given weight of water:

$$(1) \quad \frac{\text{Weight of oxygen}}{\text{Weight of hydrogen}} = \frac{32}{2 \times 2x}$$

$$(2) \quad \frac{\text{Weight of water}}{\text{Weight of hydrogen contained in it}} = \frac{32 + 4x}{4x}.$$

$$(3) \quad \frac{\text{Weight of water}}{\text{Weight of oxygen contained in it}} = \frac{32 + 4x}{32}.$$

A great many attempts to determine these ratios have been made. The earliest determination of considerable accuracy was that of

Dumas, who passed carefully purified hydrogen over heated copper oxide, forming water and copper.

The weight of oxygen in the water was given by the loss of weight of the copper oxide, while the weight of hydrogen combining with it was given by difference between the weight of water formed (absorbed by weighed U-tubes containing drying agents) and the weight of oxygen obtained as above. The accuracy of this work, described in § 196, has been much surpassed by more modern determinations.

The most accurate of these were carried out by Morley in 1895 and by Noyes in 1907. The former is described in some detail below.

Morley prepared oxygen by heating purified potassium chlorate and removed any impurities ($Cl_2$, etc.) by passing the gas through three wide horizontal U-tubes. The first was filled with glass beads, wetted with strong potassium hydroxide, the second with glass beads wetted with sulphuric acid, and the third contained phosphorus pentoxide and glass wool. The oxygen was collected in large glass globes, previously evacuated, and holding some 10–18 litres.

Hydrogen was prepared by the electrolysis of dilute sulphuric acid, the gas being passed successively through strong potash, over red-hot copper and through three long drying tubes, similar to those used for the oxygen. It is very difficult to weigh hydrogen with accuracy, for its weight is rarely more than one six-hundredth of the globe which contains it, and very small errors in weighing the globe become appreciable when their effect on the small weight of hydrogen contained in it is considered. Morley accordingly absorbed his hydrogen in the metal *palladium* (§ 1222), which will absorb up to 800 times its own volume of the gas. A tube containing palladium foil (Fig. 18) was heated to redness, and all other gases were displaced from it by a current of the pure hydrogen. The outlet from the tube was fused up and it was allowed to cool, hydrogen being absorbed. Elaborate precautions were taken to avoid leakage at the stopcock.

Both the oxygen globe and the palladium tube containing the hydrogen were weighed, with elaborate precautions to avoid errors due to variations in density of the air. Counterpoises were used to eliminate the buoyancy effect as far as possible, and the oxygen globes were enclosed in a non-conducting desiccator.

The globe containing the oxygen and the palladium tube containing the hydrogen were connected by ground-joints to an exhausted and weighed combustion tube, in which were two platinum jets (*a a*) at which the gases could burn, forming water, and two electrodes (*f f*) between which a spark could be passed to light the gases. This

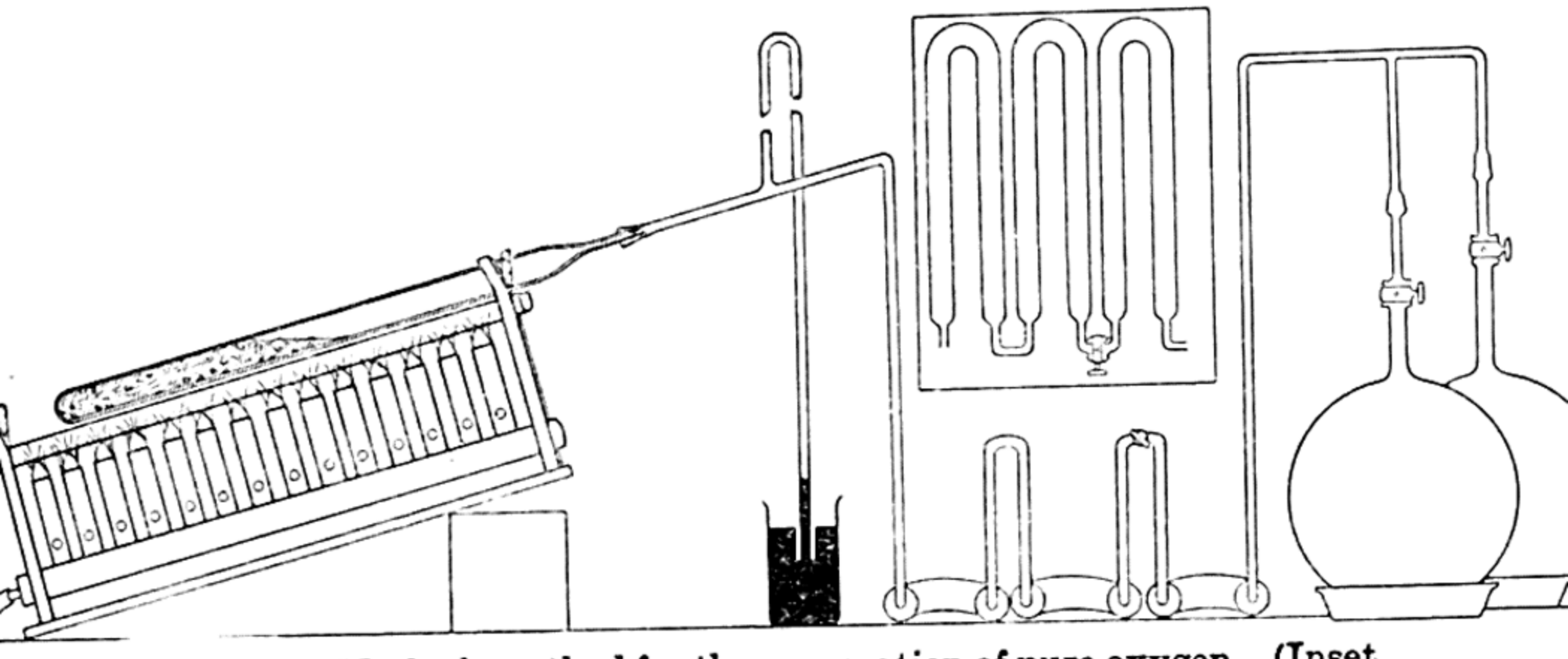


FIG. 17.—Morley's method for the preparation of pure oxygen. (Inset, plan of tubes for drying and purification of the gas.)

FIG. 18.—Tube containing palladium foil for the absorption of hydrogen.

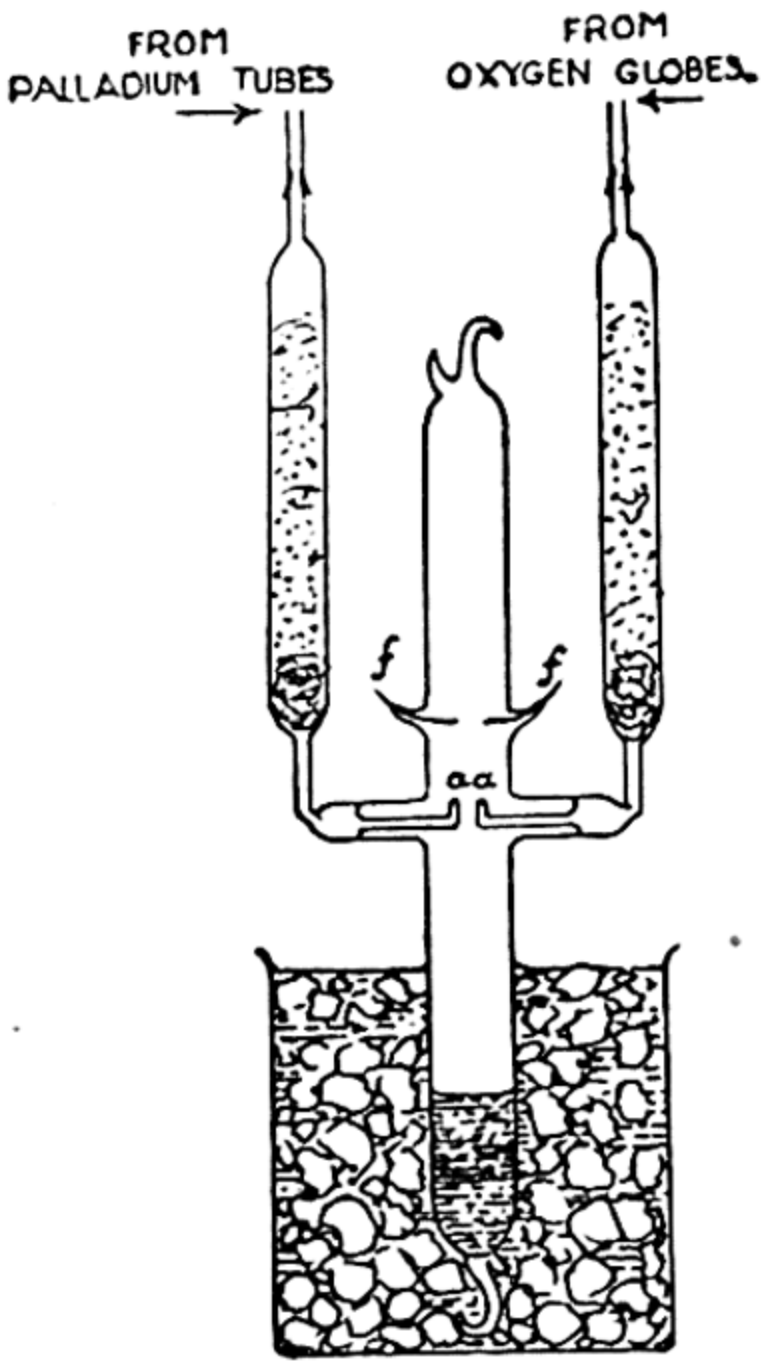



FIG. 19.—Combustion tube used by Morley for the synthesis of water.

tube (Fig. 19) was immersed in ice in order to condense the steam formed.

The gases burned and formed steam which condensed, its place being taken by more gases. The process continued until some 42 litres of hydrogen and 21 litres of oxygen had combined. The globes and palladium tube were then closed by their stopcocks. Some uncombined gas remained in the combustion chamber, and this was removed by freezing the water, cooling it to – 18° C., when its vapour pressure was negligible, and then pumping out the gas remaining. This was collected and analysed by means of a eudiometer (p. 230), and the weight of the oxygen and hydrogen it contained was deduced from density measurements and subtracted from the weights of the gases used. The combustion tube was then sealed and weighed. The globe containing oxygen and the tube containing hydrogen were weighed with great care, the differences between their weights before the experiment and after (with the correction mentioned above) giving the weights of oxygen and of hydrogen combining and the weight of the water in the combustion tube afforded a further check.

Morley found that 1·0076 gms. of hydrogen combined with 8·000 gms. of oxygen. He also determined the ratio of the densities of the gases by weighing them in globes, when he obtained a ratio, $H_2 : O_2$ of **1·0076 : 16·000** in full confirmation of his other results. As hydrogen and oxygen are both diatomic (pp. 52, 74), the ratio of the atomic weights, H : O, is the same as that of the molecular weights, $H_2 : O_2$, and by Avogadro's law, these are in the same proportions as the densities, *i.e.*, **1·0076 : 16·000**.

A very elaborate investigation was carried out by Noyes in 1908, which is of the same degree of accuracy as Morley's. It is not possible to explain the method fully, but Fig. 20 gives an idea of it. In one of the best series of experiments hydrogen and oxygen were made by electrolysis of barium hydroxide solution and purified by passing (1) through hard glass tubes containing heated platinised quartz, (2) through much caustic potash solution,

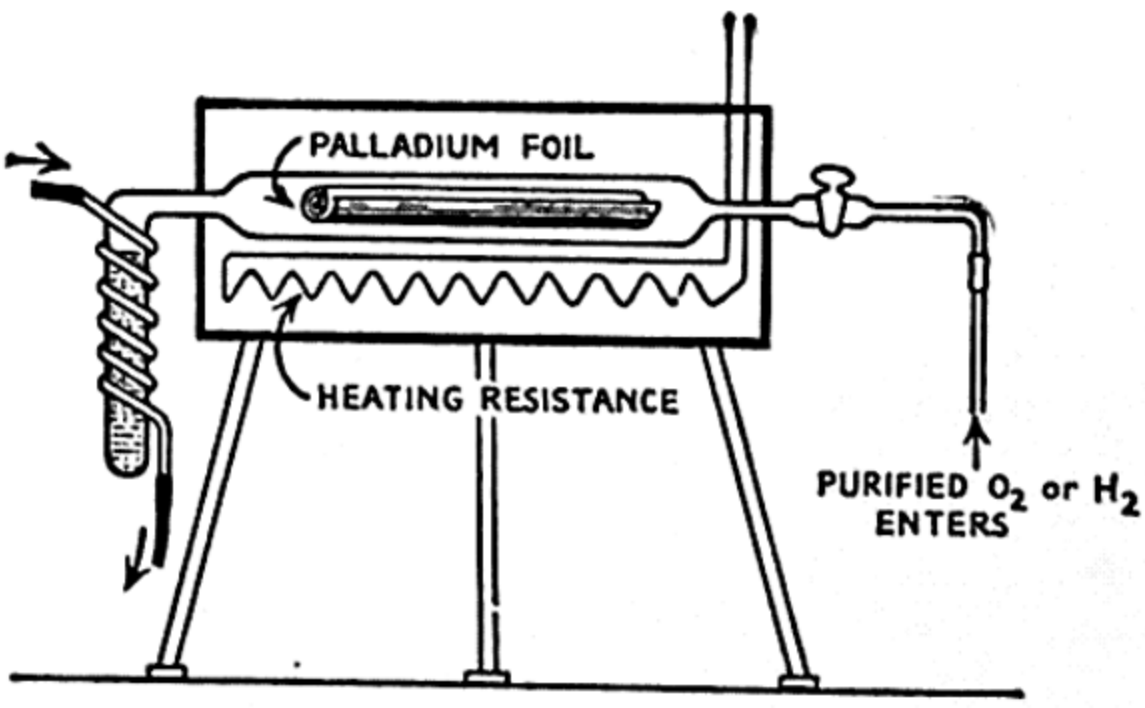



FIG. 20—Noyes' apparatus for the quantitative synthesis of water.

(3) through condensing bulbs to remove moisture, (4) over potash sticks to remove further water, (5) over phosphorus pentoxide. The hydrogen was first admitted to an exhausted tube containing cold palladium foil which absorbed about 5 gms. of it. This tube was then weighed with great care and the fullest precautions as to standardisation of weights, etc. The tube was then connected to the pure oxygen supply and the palladium heated. The hydrogen absorbed by the palladium burned and formed steam which condensed to water in the cooled limb of the tube. When combustion was complete the tube and water were weighed, thus also giving the weight of the oxygen. The residual gases left in the tube were recovered and measured and their weights allowed for. Noyes' results indicated a value of 1·0078 for the atomic weight of hydrogen. A fault in all these determinations was the fact, at that time unknown, that there are two isotopes of hydrogen $H^1$ and $H^2$ (§§ 192a, 193) and that the proportions of these in hydrogen compounds is altered by purification. Mass spectrographic methods indicate a value of 1·0081 for $H^1$ and $2{\cdot}0163_3$ for $H^2$. These figures agree better with Noyes' results than with Morley's.

**70. Atomic Weights of Silver, Nitrogen and Chlorine.**—Richards and his co-workers in America have been responsible for some of the best values for the atomic weights of these elements. These were given by (1) the determination of the weight of silver in a given weight of silver chloride; (2) the determination of the weight of silver chloride obtained from a given weight of ammonium chloride; (3) the determination of the weight of silver nitrate formed from a given weight of silver. In these three results the atomic weights of silver, nitrogen, hydrogen, oxygen and chlorine are concerned. If we take oxygen as standard 16·000, and the very accurate value for hydrogen of 1·0076 (Morley) there remain three unknown quantities, and we can obtain three equations (p. 80), so that all the atomic weights of silver, nitrogen and chlorine are directly known in terms of those of hydrogen and oxygen and are independent of each other or of any other determination.

(1) Silver was prepared by reduction of silver nitrate, which had been fifteen times re-crystallised, and was fused on lime in an atmosphere of hydrogen (p. 310). This silver was treated with the purest nitric acid and the solution so obtained was diluted and precipitated by highly purified common salt solution. The precipitate of silver chloride was filtered off through a Gooch crucible, carefully washed, dried and weighed with the most refined precautions. 1·00000 gm. of silver yielded 1·32867 gms. of silver chloride.

(2) Ammonium chloride was prepared in two ways. Ammonium sulphate was treated with permanganate in acid solution to oxidise organic matter. Ammonia gas was prepared from it by means of pure lime and was condensed in the purest hydrochloric acid. The solution was evaporated and the product sublimed.

Another sample was prepared from ammonium sulphate obtained in a manner as different as possible, *i.e.*, by the electrolytic reduction of nitric acid.

The ammonium chloride was weighed out with suitable precautions and silver nitrate prepared as above was added. The precipitate of silver chloride was treated as above and weighed. 1·00000 gm. of silver chloride was precipitated by 0·373217 gm. of ammonium chloride.

(3) Very pure silver nitrate was prepared from nitric acid repeatedly

redistilled and silver prepared by reduction of silver nitrate previously fifteen times recrystallised. The silver was dissolved in the acid (diluted with very pure water) in a small quartz flask, and the liquid evaporated to dryness in a gentle current of air. 1·00000 part of silver yielded 1·57497 parts of silver nitrate.

The three ratios obtained as above give us three of the most important atomic weights. To quote Richards's own words (*Chem. News*, Vol. 99, p. 77):

"The relation of these results to other atomic weights is very far-reaching and important. Clearly, they connect the atomic weight of nitrogen with that of hydrogen, silver and chlorine, and therefore, with the help of other well-known relations, affect the atomic weight of each of these elements in relation to each other. The calculation is very simply carried out as follows: Let—

$$\frac{AgCl}{Ag} = a \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{NH_4Cl}{AgCl} = b \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{AgNO_3}{Ag} = c \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

"The three atomic weights supposed to be unknown may be designated as follows: Ag = $x$, Cl = $y$, N = $z$. From the work of Morley, hydrogen may be taken as 1·0076 if oxygen = 16 (ref. pp. 73, 75). Substituting these values in Equations 1, 2 and 3 we obtain the following:

$$x + y = ax \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$y + z + 4{\cdot}0304 = b\,(x + y) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$x + z + 48{\cdot}000 = cx \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

"Substituting in Equation 5 the value of $z$ as found from Equation 6 we have:

$$(c - 1)\,x - bx + (1 - b)\,y = 43{\cdot}9696,$$

but according to Equation 4, $y = (a - 1)\,x$; hence—

$$x = \frac{43{\cdot}9696}{c - 1 - b + (1 - b)\,(a - 1)} \quad . \quad . \quad . \quad (7)$$

The values $a$, $b$ and $c$ are all known . . ."

These are the ratios found by Richards and his co-workers, and discussed in paragraphs 1, 2, 3 above.

"$a$ (the quantity of silver chloride obtained from 1 gm. of silver) was found by Richards and Wells to be 1·32867 . . . $c$ (the quantity of silver nitrate obtained from the same quantity of silver) was found by Richards and Forbes to be 1·57479 . . . The present investigation gives the value of $b$ [1] as 0·373217 . . .

"Substituting these values in Equation 7 we obtain $x$ the atomic weight of silver = 107·881.

"Substituting this value in Equation 4, we obtain $y$, the atomic weight of chlorine, = 35·4574, and substituting these values in Equations 5 or 6, we obtain $z$, the atomic weight of nitrogen, = 14·0085. These three values for the atomic weights of silver, chlorine and nitrogen are entirely independent

[1] The weight of ammonium chloride required to produce 1 gm. of silver chloride.

of any but the most recent work, and rest directly, through silver nitrate and water, upon the international standard of atomic weight O = 16·000."

It should not be thought that the above are the only accurate determinations of these atomic weights. Many others have been performed and are in varying degrees of agreement with them and each other. The International Committee of Atomic Weights is a body which at intervals reviews the total of atomic weight determinations and fixes on the figures they consider the most probable for each element.

For the above five fundamental elements the most recent and probable values are :

| | |
|---|---|
| Hydrogen . . . . | 1·0080 |
| Oxygen . . . . | 16·000 (Standard) |
| Nitrogen . . . . | 14·008 |
| Chlorine . . . . | 35·457 |
| Silver . . . . | 107·880 |

## Calculations Based on Atomic Weights

The meaning of chemical formulæ and equations has been explained in Chapter II. The great importance of chemical equations lies not so much in their being a convenient symbol to express the nature of the reagents and products in a chemical change, as in the fact that all chemical calculations are based on the use of formulæ and equations in conjunction with atomic weights.

**71. Determination of Formulæ.**—The formula of a compound expresses the number and kind of atoms present in its molecule, and in general is determined from four sets of data.

(1) The knowledge of what elements are contained in the compound.

(2) The percentage composition of the compound, or other indication of the proportion by weight in which these elements are present.

(3) The atomic weights of the elements concerned.

(4) The molecular weight of the compound.

(1) To discover what elements are present in a compound is not as a rule difficult. The methods of Qualitative Analysis, by which these elements are converted into easily recognisable substances, are used.

(2) The percentage composition of the compound is arrived at by Quantitative Analysis. The elements in a known weight of the compound are converted into some form in which they can be separated and weighed. Numerous examples of the process are to be found in the succeeding pages.

(3) The atomic weights of the elements are usually obtainable from tables. Difficulty might be found in the case of

new elements, and in such a case they would have to be determined by the methods of §§ 61–68.

(4) Calculations from the above data will give the simplest possible formula, which indicates correctly the proportions of the atoms in the molecule, but does not give their actual numbers. The molecular weight of the compound will indicate this, as also may evidence derived from its chemical behaviour.

The method of procedure is best illustrated by the study of a simple case.

*A volatile liquid compound has the percentage composition :*

*Carbon*, 10·05 *per cent.* ; *Hydrogen*, 0·84 *per cent.* ; *Chlorine*, 89·11 *per cent. The density of its vapour referred to hydrogen is* 59. *Calculate its formula.*

The atomic weights of carbon, hydrogen and chlorine may be taken as 12, 1, and 35·5 respectively. In order to find the numbers of atoms in the weights of carbon, hydrogen and chlorine we must divide the total weight of atoms of each kind (given by the percentage composition) by the weight of one atom (the atomic weight).

The relative number of atoms in the compound are then :

$$\text{Carbon} \quad . \quad . \quad . \quad . \quad . \quad \frac{10{\cdot}05}{12}$$

$$\text{Hydrogen} \quad . \quad . \quad . \quad . \quad \frac{0{\cdot}84}{1}$$

$$\text{Chlorine} \quad . \quad . \quad . \quad . \quad \frac{89{\cdot}11}{35{\cdot}5}$$

The formula then is some multiple of

$$\underset{12}{\overline{C_{10\cdot05}}} \quad \underset{1}{\overline{H_{0\cdot84}}} \quad \underset{35\cdot5}{\overline{Cl_{89\cdot11}}}$$

$$= C_{0\cdot84} \quad H_{0\cdot84} \quad Cl_{2\cdot51}$$

Dividing these figures by 0·84 the formula becomes

$$C_1H_1Cl_{2\cdot99} \text{ or } CHCl_3.$$

But the formula may be equally $C_2H_2Cl_6$ or $C_4H_4Cl_{12}$ or $C_nH_nCl_{3n}$, as all these would agree equally well with the above percentage composition and atomic weights.

If the compound has the formula, $CHCl_3$ it has the molecular weight $12 + 1 + 3 \times 35{\cdot}5 = 119{\cdot}5$, while if the formula is $(CHCl_3)_n$ the molecular weight will be $119{\cdot}5\ n$.

The vapour density of the compound was found to be approximately 59, and its molecular weight (§ 50) should therefore be 118, which evidently indicates that the correct value is 119·5, not

$2 \times 119{\cdot}5$ or any higher multiple. The formula is therefore $CHCl_3$.

The formulæ of gases may often be calculated from the volumes of gaseous products, which they form or from which they are formed in chemical reactions, thus avoiding the tedious process of weighing gases. This process is again best illustrated by an actual example.

*Two cubic centimetres of a gas containing only hydrogen and carbon were mixed with an excess of oxygen* (30 c.c.) *in a eudiometer. After passing an electric spark, causing combustion to occur, the mixture became reduced in volume to* 25 *c.c. On adding some caustic soda solution the volume further diminished to* 17 *c.c., the residue being pure oxygen.*

Suppose the formula of the gas to be $C_xH_y$. Then when it combines with oxygen to form carbon dioxide and water the equation will be

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 = xCO_2 + \frac{y}{2} H_2O.$$

1 molecule. $x + \frac{y}{4}$ molecules $= x$ molecules. $\frac{y}{2}$ molecules.

By Avogadro's law equal numbers of molecules are contained in equal volumes of gases under the same conditions of temperature and pressure. So it follows that 1 volume of a hydrocarbon gas, $C_xH_y$, reacts with $x + \frac{y}{4}$ volumes of oxygen, forming $x$ volumes of carbon dioxide and $\frac{y}{2}$ volumes of steam.

When the mixture cools the steam will condense. The alteration in volume will be a *diminution* due to the disappearance of the hydrocarbon gas (1 vol.) and the oxygen which reacts with it $\left(x + \frac{y}{4}\right)$ vols. and also an *increase* due to the production of carbon dioxide. The water vapour can be neglected, for it condenses to a negligible volume, and so may be regarded as if it had not been formed at all.

The total diminution will then be

$$1 + x + \frac{y}{4} - x$$

$$= 1 + \frac{y}{4} \text{ vols.}$$

and the further diminution when the carbon dioxide is absorbed by caustic soda will be $x$ vols. Now, in the actual experiment the quantity of hydrocarbon taken (1 vol.) = 2 c.c.

The first diminution in volume was 7 c.c., and the second was 8 c.c.



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Thus $$2\left(1+\frac{y}{4}\right)=7 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

$$2+\frac{y}{2}=7$$

$$y=10.$$

$$2x=8 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

$$x=4$$

Formula of gas $= C_4H_{10}$.

In some cases the density of a gas alone is enough to give the formula. Thus, for example, the density of nitrous oxide referred to hydrogen is 22.

If the density of the gas is 22 its molecular weight is 44. Since the atomic weight of nitrogen is 14 and that of oxygen 16 and both elements are contained in the gas there cannot be more than two atoms of either element in the molecule. The only possible formulæ are—

$N_2O$ giving M.W. 44
$NO_2$ giving M.W. 46
$NO$ giving M.W. 30.

Clearly the first is the only formula which agrees with the experimentally found value of 44. This method is applicable to most simple compounds, but with more complex ones the accuracy of ordinary density determinations is not sufficient to discriminate between the possible values which may lie very close to each other.

**72. Calculations derived from the Formula.**—Since the formula of a compound represents the numbers of atoms which its molecule contains, and since the atomic weights are the relative weights of these atoms, it is easy to obtain from the formula of a compound the weights of the various elements contained in a given weight of it.

*Example* 1.—*Calculate the percentage composition of potassium permanganate* $KMnO_4$ (*atomic weights* $K = 39$, $Mn = 55$, $O = 16$).

| | | |
|---|---|---|
| One atom of potassium | 39 | units of weight. |
| One atom of manganese | 55 | ,, ,, |
| Four atoms of oxygen | 64 | ,, ,, |
| are contained in one molecule of potassium permanganate | 158 | ,, ,, |

$\therefore$ in 100 units of weight of potassium permanganate there are

$$\frac{39\times 100}{158}$$ units of weight of potassium.

$\frac{55 \times 100}{158}$ units of weight of manganese.

$\frac{64 \times 100}{158}$ units of weight of oxygen.

∴ Percentage composition is—

| | |
|---|---|
| K . . . . . | 24·7 per cent. |
| Mn . . . . . | 34·8 ,, |
| O . . . . . | 40·5 ,, |

*Example 2.—Ten grams of iron are completely converted into crystallised ferrous sulphate, $FeSO_4.7\,H_2O$. What weight of the latter salt is formed?* ($Fe = 56$, $S = 32$, $O = 16$, $H = 1$.)

One atom of iron, Fe, is contained in one molecule of ferrous sulphate, $FeSO_4.7H_2O$.

∴ 56 units of weight of iron are contained in $56 + 32 + (4 \times 16) + 7\,(16 + 2) = 278$ units of weight of crystallised ferrous sulphate.

∴ 10 gms. of iron can be converted into $\frac{278 \times 10}{56}$ gms. crystallised ferrous sulphate = 49·6 gms.

**73. Equations.**—An equation can be written for every chemical change, and it is impossible for the ordinary chemist to burden his mind by remembering all the equations he will ever need. It is important then to be able to work out equations when required.

In order to write the equation for a chemical change, we require to know the formulæ of the reagents and the products, and from these the equation may be worked out either by trial and error or mathematically. Our guide in writing the equation is the fact that no atoms are destroyed or created in a chemical change. A correct equation must therefore "balance," *i.e.*, have on each side the same number of each kind of atom.

Let us suppose that we require the equation representing the burning of iron pyrites $FeS_2$ in oxygen $O_2$, forming ferric oxide $Fe_2O_3$, and sulphur dioxide $SO_2$.

$$nFeS_2 + mO_2 = pFe_2O_3 + qSO_2.$$

We must have at least two molecules of iron pyrites to provide the two iron atoms needed for $Fe_2O_3$. We may then write

$$2FeS_2 + mO_2 = Fe_2O_3 + 4SO_2.$$

Adding the oxygen atoms on the right-hand side we find eleven, which requires $5\frac{1}{2}O_2$. As half-molecules are excluded we must multiply

$$2FeS_2 + 5\tfrac{1}{2}O_2 = Fe_2O_3 + 4SO_2$$

by two giving

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

In difficult cases equations may be written for successive stages of the reaction, real or hypothetical, and these may be added together (*cf.* pp. 743, 744).

**74. Calculation of the Quantities involved in a Chemical Reaction.**—The equation for a chemical change represents the rearrangement of the atoms which compose the molecules taking part in the reaction. Since the weights of these atoms remain constant it is easy to discover the weights of the various products.

Thus for example, in an equation such as

$$ZnSO_4 + 2NaOH = Na_2SO_4 + Zn(OH)_2$$

the weights of the reacting substances and products are given by substituting the relative weight of each atom for its symbol.

| | | |
|---|---|---|
| $ZnSO_4$ | + | $2NaOH$ |
| $65+32+(4\times16)$ parts by weight of zinc sulphate. | react with | $2(23+16+1)$ parts by weight of caustic soda. |
| $= Na_2SO_4$ | + | $Zn(OH)_2$ |
| forming $2\times23+32+(4\times16)$ parts by weight of sodium sulphate. | and | $65+2(16+1)$ parts by weight of zinc hydroxide. |

Adding these weights we find that 161 parts of zinc sulphate react with 80 parts of caustic soda, forming 142 parts sodium sulphate and 99 parts of zinc hydroxide.

If we take these parts by weight to be grams, then the total for each single molecule will be its gram-molecular weight. Now the gram-molecular weight of any gas at N.T.P. occupies 22·4 litres (§ 49), and we can in this way obtain from the equation not only weights of reacting substances but also the volumes of any gases taking part in the change. Thus, consider the reaction between sulphuric acid and carbon, yielding water and the gases carbon dioxide and sulphur dioxide, symbolised by the equation

$$2H_2SO_4 + C = CO_2 + 2SO_2 + 2H_2O.$$

From this equation we can deduce that

| | | |
|---|---|---|
| $2H_2SO_4$ | + | $C$ |
| $2(2+32+4\times16)$ gms. of sulphuric acid. | react with | 12 gms. of carbon. |
| $= CO_2$ | + | $2SO_2$ |
| forming one gram-molecule of carbon dioxide, 44 gms. and 22·4 litres at N.T.P. | and | two gram-molecules, 128 gms. and 44·8 litres of sulphur dioxide. |
| | + | $2H_2O$ |
| | and | $2(2+16)=36$ gms. of water. |

A few examples of calculations based on equations may be helpful.

(1) *What weight of iodine is liberated by the action of* 1·10 *gms. of bromine on an excess of potassium iodide solution ?* (*Br* = 80, *K* = 39, *I* = 127.)

$$Br_2 + 2KI = 2KBr + I_2.$$

2 × 80 gms. bromine form . . 2 × 127 gms. iodine.

∴ 1·1 gms. bromine form . . $\frac{2 \times 127 \times 1{\cdot}1}{2 \times 80}$ gms. iodine.

$= 1{\cdot}75$ gms.

(2) *What weight of anhydrous sodium sulphate and what volume of sulphur dioxide at* 10° *C. and* 750 *mm. pressure can be obtained by the action of strong sulphuric acid on* 10 *gms. of crystallised normal sodium sulphite,* $Na_2SO_3.7H_2O$ *?*

The equation is

$$\underset{\substack{(2\times23)+32+48+7\,(2+16)\\ \text{gms. sodium sulphite.}}}{Na_2SO_3.7H_2O} + H_2SO_4 = \underset{\substack{\text{yield } (2\times23)+32+4\times16\\ \text{gms. sodium sulphate.}}}{Na_2SO_4} + 8H_2O + \underset{\substack{\text{and } 22{\cdot}4 \text{ litres}\\ \text{of sulphur di-}\\ \text{oxide at S.T.P.}}}{SO_2}.$$

Then 10 gms. sodium sulphite yield (*a*) $\frac{142 \times 10}{252}$ gms. sodium sulphate and (*b*) $\frac{22{\cdot}4 \times 10}{252}$ litres of sulphur dioxide at S.T.P.

(*a*) Weight of sodium sulphate produced = 5·63 gms.

(*b*) Volume of sulphur dioxide at 10° C. and 750 mm. will be

$$\frac{22{\cdot}4 \times 10 \times 760 \times 283}{252 \times 750 \times 273} \text{ litres.}$$

$= 934$ c.c.

(3) *What weight of silver chloride is precipitated when* 105 *c.c. of hydrogen chloride, measured at* 15° *C. and* 770 *mm. pressure, are absorbed by silver nitrate solution ?* (*H* = 1, *Ag* = 108, *N* = 14, *O* = 16, *Cl* = 35·5.)

$$\underset{\text{22·4 litres at N.T.P.}}{HCl} + AgNO_3 = \underset{\text{precipitate}}{AgCl} + \underset{\text{108+35·5 gms. silver chloride.}}{HNO_3}$$

105 c.c. of hydrogen chloride at 15° C. and 770 mm. pressure is equivalent to

$$\frac{105 \times 273 \times 770}{288 \times 760} \text{ c.c. at S.T.P.}$$

22,400 c.c. hydrogen chloride at N.T.P. precipitate 143·5 gms. silver chloride.

And so $\frac{105 \times 273 \times 770}{288 \times 760}$ c.c. will precipitate

$$\frac{143{\cdot}5 \times 105 \times 273 \times 770}{22400 \times 288 \times 760}$$

$= 0{\cdot}646$ gm. silver chloride.

Nearly all chemical calculations are variants of the above types.

## CHAPTER IV

## SOLUTION AND CRYSTALLISATION

**75. Suspensions and Solutions.**—In Chapter II. we have distinguished between pure substances and mixtures. There exists, however, one particular class of mixture which is of such importance that it requires separate consideration.

A mixture of a solid and a liquid (or of two liquids) may be of three types which, as we shall see, pass imperceptibly into each other.

(1) *True solutions*, which consist of single molecules suspended in the liquid solvent. The dissolved substance cannot be separated from the solution either by the action of gravity or any form of filtration as ordinarily understood.[1]

(2) A *colloidal solution*, consisting of larger particles, which may be single molecules or aggregates of molecules suspended in a liquid. These may or may not be visible under the microscope. They are electrically charged and do not settle out as a result of the action of gravity, but filtration through a very fine membrane of collodion may separate the particles.

(3) A *suspension* consisting of gross particles of solid (containing many millions of molecules) surrounded by the fluid. The solid may be separated from these by filtration or by the action of gravity.

**76. The Nature of True Solutions.**—The vast majority of substances, whether solids, liquids or gases, *dissolve* in some liquid under some conditions.

Consider what happens when a soluble solid, such as potassium dichromate, for example, is added gradually to water at 15° C., the whole being well stirred. The particles of solid potassium dichromate disappear, the water receiving at the same time their colour and so becoming orange. The process continues until 100 gms. of the water have dissolved 9·6 gms. of the salt, when the action ceases and no more of the salt dissolves. If the temperature is now raised to 30° C. a further 8·5 gms. of potassium dichromate are dissolved and then, as before, the process ceases.

Very similar phenomena occur on adding a liquid (say, bromine) to another liquid (say, water), with which it cannot be mixed in all

[1] But see § 56 on semipermeable membranes.

proportions. This case is a little more complicated, for the bromine dissolves in the water and the water in the bromine, forming two solutions which do not mix. A gas also dissolves in a liquid in a similar manner, the gas being dissolved only until a solution of a certain strength has been formed.

A solution, which at a given temperature will dissolve no more of a substance however long it remains in contact with it, is said to be *saturated* with that substance at the temperature in question.

The liquid in which the substance is dissolved is called the *solvent*, and the dissolved substance the *solute*. There is no real distinction between the two. Thus, in a 50 per cent. solution of alcohol in water we may with equal truth say that the alcohol is dissolved in the water, or the water in the alcohol.

An investigation of the properties of solutions reveals certain fundamental facts.

(1) *When a substance is dissolved in a liquid it becomes evenly distributed through the liquid, and once so distributed it will not settle out by the action of gravity, etc.*

If a piece of a soluble solid is placed at the bottom of a vessel of water it dissolves and forms a strong solution at the bottom of the vessel. The solid contained in the strong solution slowly diffuses upwards until in the course of, it may be years, the solution becomes of the same concentration throughout. If the solution is stirred it soon becomes of even concentration throughout. The fact that the whole of volumetric analysis is based on the assumption that a dissolved substance remains distributed evenly through a solution is a sufficient demonstration of the truth of this principle.

(2) *When a substance dissolves in a liquid, the solution has physical and chemical properties which, while they are not identical with those of the solute and solvent, show a close resemblance to them.*

A close physical or chemical resemblance between a solid and a solution is not to be expected, for their molecular structure is very markedly different (§ 41). Dry solid salts rarely react, except under great pressure, while solutions of salts commonly react with great ease and rapidity. In practice we study the chemical properties of solutions so much more frequently than the chemical properties of solids that these differences in behaviour between dissolved and undissolved solids are apt to go unobserved.

The chemical properties of a dissolved substance have in general a fairly close analogy to those of the substance in the form of a gas or a liquid, which must incline us to the view that solutions are mixtures, not chemical compounds.

Certain classes of substances, namely acids, alkalis and salts, are *ionised* in solution, that is to say broken up into two or more

electrically charged atoms or groups of atoms. This is a chemical change, and so it is to be expected that the properties of their solutions should differ somewhat from those of the solid compounds. Such solutions are discussed in Chapter VI.

(3) *The solute can be recovered unchanged from the solution by evaporation, changes of temperature, or other means.*

Thus, if a saturated solution of copper sulphate is cooled or is left to evaporate, crystals of the salt appear. The energy required to remove the dissolved substance from the solution is not very great.

This fact, taken with (2) above, and with the fact that their composition can vary within limits, makes us suppose that solutions are mixtures and not chemical compounds.

**77. Saturated Solutions.**—We have seen already that, at a given temperature, no more than a certain weight of a solid can be dissolved in a given weight of liquid. This is true also of some liquids, but not of all. Thus at 15° C. a maximum of 3·5 gms. of bromine can be dissolved in 100 gms. water, but on the contrary, sulphuric acid and water can be mixed in any proportion. Solutions which have been in contact with the solute until no more can be dissolved, are called saturated solutions, and are best defined as follows :

**A solution is said to be saturated at a given temperature when it is in equilibrium with the solute at that temperature.**

Thus, if a piece of copper sulphate is placed in a saturated solution of copper sulphate no apparent change takes place. If placed in a weaker (*unsaturated*) solution at the same temperature it will dissolve ; if placed in a stronger (*supersaturated*) solution at the same temperature solid copper sulphate will be deposited upon it.

The notion of equilibrium in this case is perhaps more clearly grasped if an attempt is made to visualise what is happening when a solution and a solid are in contact. Two phenomena are continually taking place. In the first place, molecules of the solid are being carried from its surface into the liquid, and in the second place, molecules suspended in the liquid are being deposited again on the surface of the solid. When the solution is unsaturated the first process predominates and molecules leave the solid more quickly than they are deposited on it. In a supersaturated solution molecules are deposited on the solid more quickly than they leave it. In a saturated solution the rates of solution and deposition are equal, *i.e.*, there is an equilibrium between the dissolved solute and undissolved solute.

**78. Solubility.**—The solubility of a solute in a solvent at a given temperature is a number expressing the quantity of the solute which has to be dissolved in a given quantity of solvent at that temperature

in order to form a saturated solution. It is, in fact, the concentration (or 'strength') of a saturated solution. The solubility is commonly expressed as

(1) Grams of solute per 100 gms. solvent.

(2) Grams of solute per 100 gms. solution.

Thus the solubility of copper sulphate at 15° C. is 40 *gms. per* 100 *gms. water*. This is equivalent to 40 gms. per 140 gms. solution, *i.e.*, 28·6 *gms. per* 100 *gms. solution.*

The solubility of gases is commonly expressed as the number of volumes of the gas dissolved at a given temperature and pressure by 1 (or 100) volumes of water.

The solubility of every substance varies with the temperature, and these variations are of great importance for the study of fractional crystallisation, the chief means by which solid chemical substances are purified.

**79. Determination of the Solubility of a Solid or Liquid.**—The

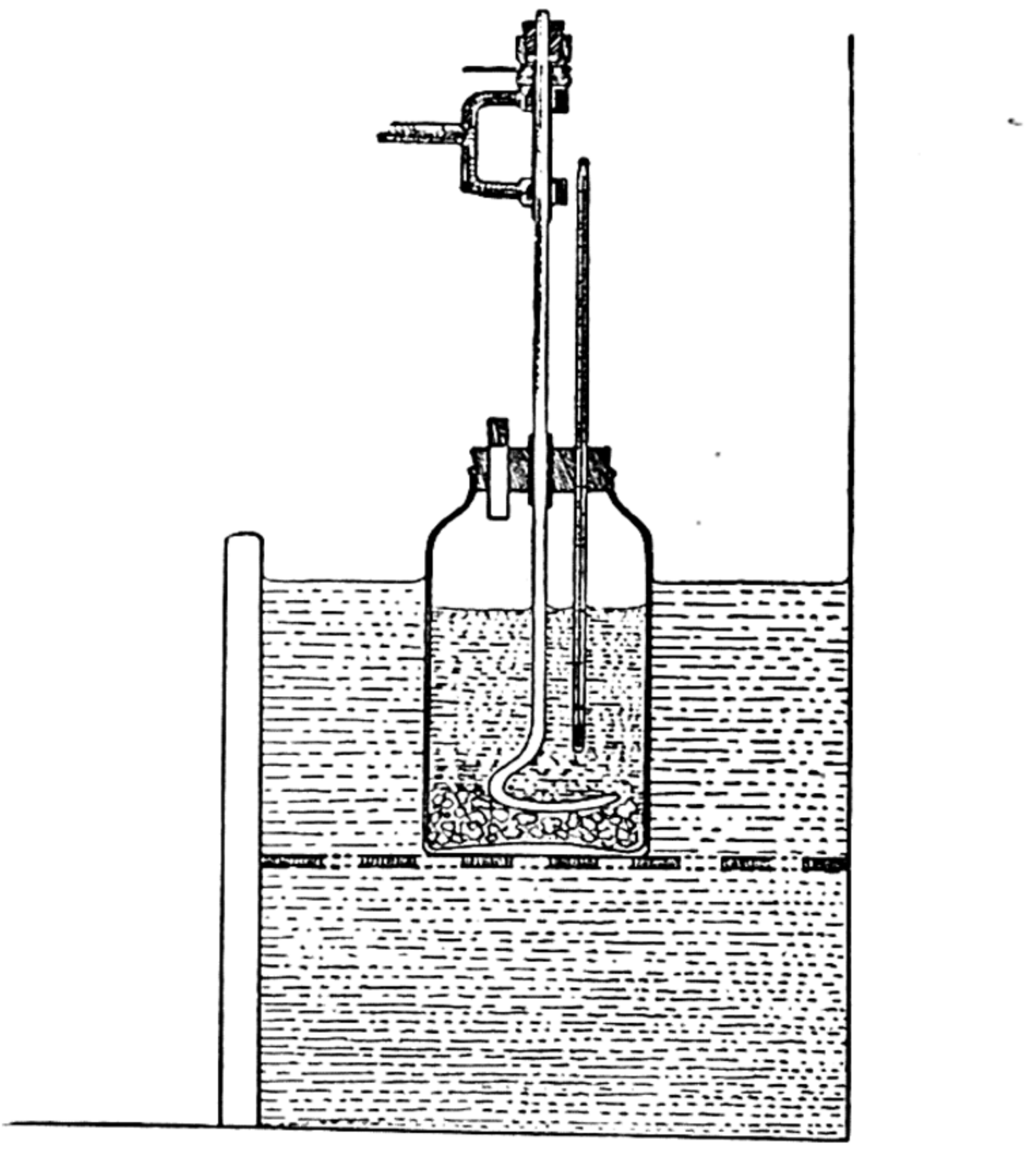


FIG. 21.—Determination of the solubility of a solid.

usual method of determining the solubility of a substance is to prepare a saturated solution of it at a fixed temperature, and to analyse

a known weight of the solution so prepared. An excess of the finely-powdered solid may be placed in a bottle provided with a thermometer, a mechanical stirrer and a tube through which a pipette may be inserted. Distilled water, previously warmed to the required temperature, is added, and the bottle placed in a thermostat where the water and solid are vigorously agitated for some two hours or, if great accuracy is sought, for an even longer period. The stirring is then stopped, and when the solid has settled out, a pipette, warmed to a little above the thermostat temperature and fitted with a filter, is used to withdraw some of the liquid, which is transferred to a weighed vessel. The vessel and liquid are then weighed and the liquid may be analysed chemically or carefully evaporated to dryness, the weight of solute in a known weight of solution being thus obtained. An example of the method used to calculate the solubility of a salt from data of this kind is given below.

*Example.—In a certain determination of the solubility of sodium chloride at* 20°c.,10·705 *gms. of the saturated solution were removed and diluted to* 500 *c.c. with distilled water. Twenty cubic centimetres of this solution, titrated with* N/10 *silver nitrate solution, required* 19·30 *c.c. of the latter.*

$$NaCl + AgNO_3 = AgCl + NaNO_3.$$

A N/10 solution contains one-tenth of an equivalent of solute per litre of solution.

19·3 c.c. of N/10 silver nitrate solution contain $\frac{19{\cdot}3}{10{,}000}$ equivalents of silver nitrate.

∴ 20 c.c. of the diluted sodium chloride solution contain $\frac{19{\cdot}3}{10{,}000}$ equivalents of sodium chloride.

∴ 500 c.c. of the standard sodium chloride solution contain $\frac{500 \times 19{\cdot}3}{20 \times 10{,}000}$ equivalents.

$$= \frac{500 \times 19{\cdot}3 \times 58{\cdot}5}{20 \times 10{,}000} \text{ gms. NaCl.}$$

∴ 10·705 gms. sodium chloride solution saturated at 20° C. contain

$$\frac{500 \times 19{\cdot}3 \times 58{\cdot}5}{20 \times 10{,}000} \text{ gms. NaCl} = 2{\cdot}823 \text{ gms. NaCl.}$$

∴ 10·705 — 2·823 gms. water dissolve 2·823 gms. salt.

∴ 7·882 gms. water dissolve 2·823 gms. salt.

∴ 100 gms. water dissolve $\frac{2{\cdot}823 \times 100}{7{\cdot}882} = 35{\cdot}8$ gms.

The solubility of common salt at 20° C. is therefore 35·8 gms. per 100 gms water.

**80. Determination of the Solubility of a Gas in a Liquid.**—The solubility of a gas (if it is not exceedingly soluble) is best determined by

means of the absorption pipette shown in Fig. 22. A gas-burette G is filled with the moist gas *vid* the three-way tap T, and the volume of the gas is read off after levelling. To the other arm of this tap an absorption pipette is connected by a spiral of metal[1] tubing (flexible enough to allow of shaking). The pipette is completely filled with air-free water by exhausting it by means of a pump and then allowing water to enter by the tap R. The volume ($v$) of the pipette is known. The gas-burette is then put into communication with the absorption pipette and by raising the levelling tube and opening the tap R some water is expelled from the pipette into a flask, thus leaving a space S filled with the gas. By weighing the water expelled its volume $v_1$ is obtained. The volume of water in the pipette is now $v - v_1$ and the volume of the space S is $v_1$. The pipette is then placed in a thermostat at the temperature at which the solubility of the gas is required and is shaken occasionally until no more gas is absorbed, atmospheric pressure being maintained by raising the levelling tube.

The volume of gas absorbed is given by the difference of the burette readings ($v_2$) less the volume of the gas in the pipette $v_1$ reduced to normal pressure and the temperature of the thermostat. The volume of water is $v - v_1$ c.c. The solubility is obtained by calculating the number of volumes of gas absorbed by 1 volume of water.

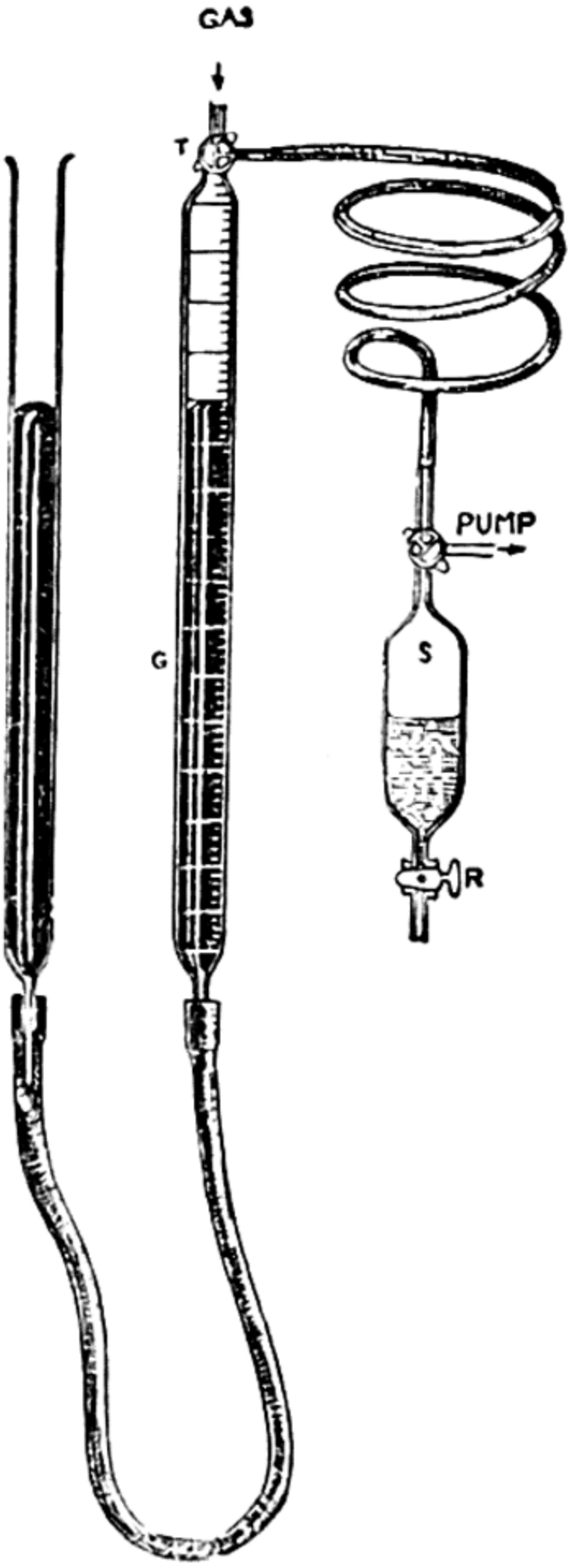



FIG. 22.—Determination of the solubility of a gas in a liquid.

**81. Solubility Curves.**—If the solubility of a substance is plotted against the temperature, the *solubility curve* is obtained. The interpretation of these is very useful in all problems concerned with the crystallisation of solids from solution and is consequently of great importance to the chemical manufacturer, who manufactures or purifies most solid substances by processes of crystallisation.

The commonest types of solubility curve (at temperatures above 0° C.) for a solid and a liquid which do not combine, are shown in Fig. 23 (A). Both the solubility and the rate of increase of solubility become greater as the temperature becomes higher.

Much more rarely the solubility curve is retrograde, *i.e.*, the solubility decreases with temperature. Such a curve is shown in Fig. 24.

[1] Many gases leak through rubber to an appreciable extent.

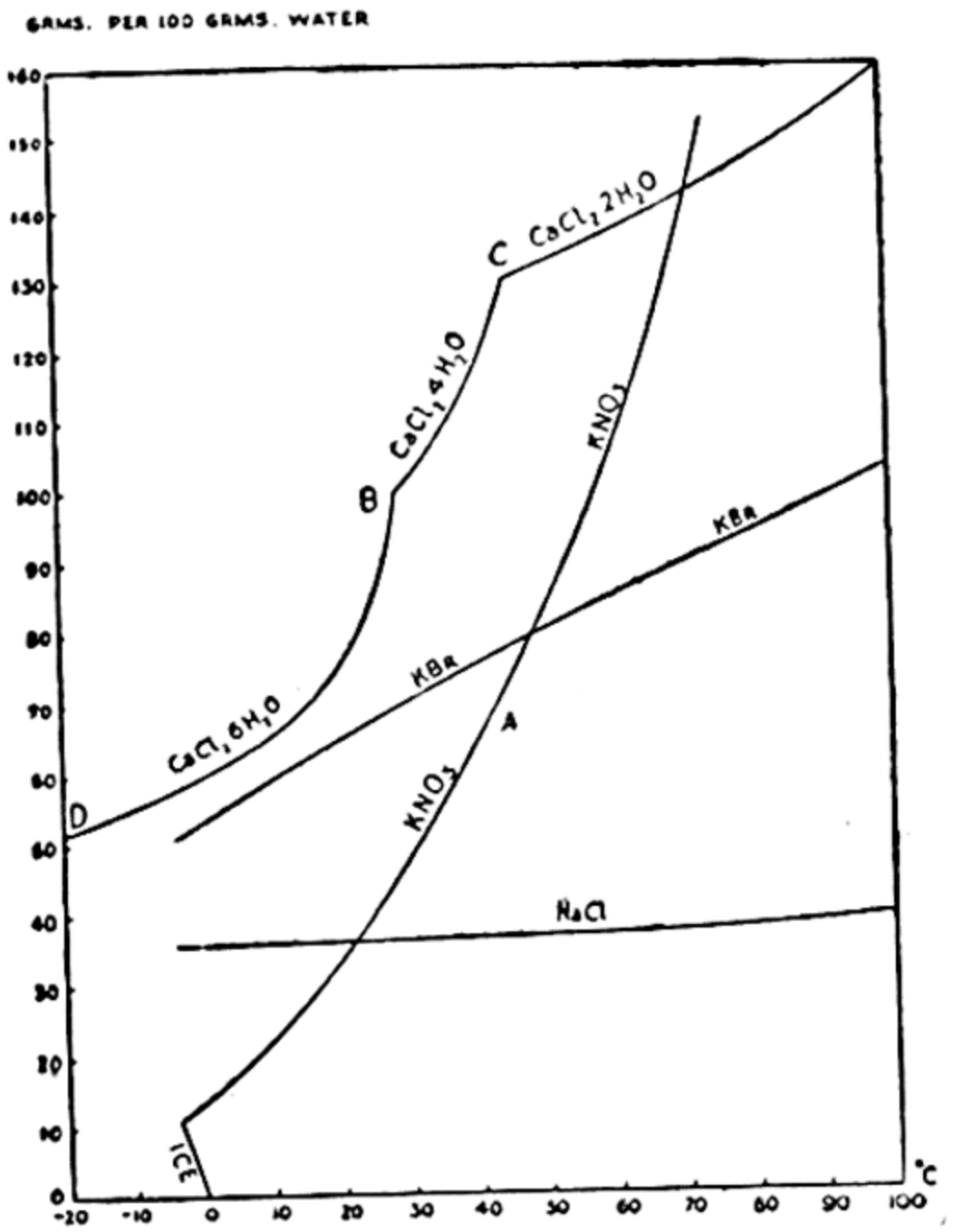



FIG. 23.—Solubility curves of certain salts.

Gms. $Ca(OH)_2$
per 100 gms. water.

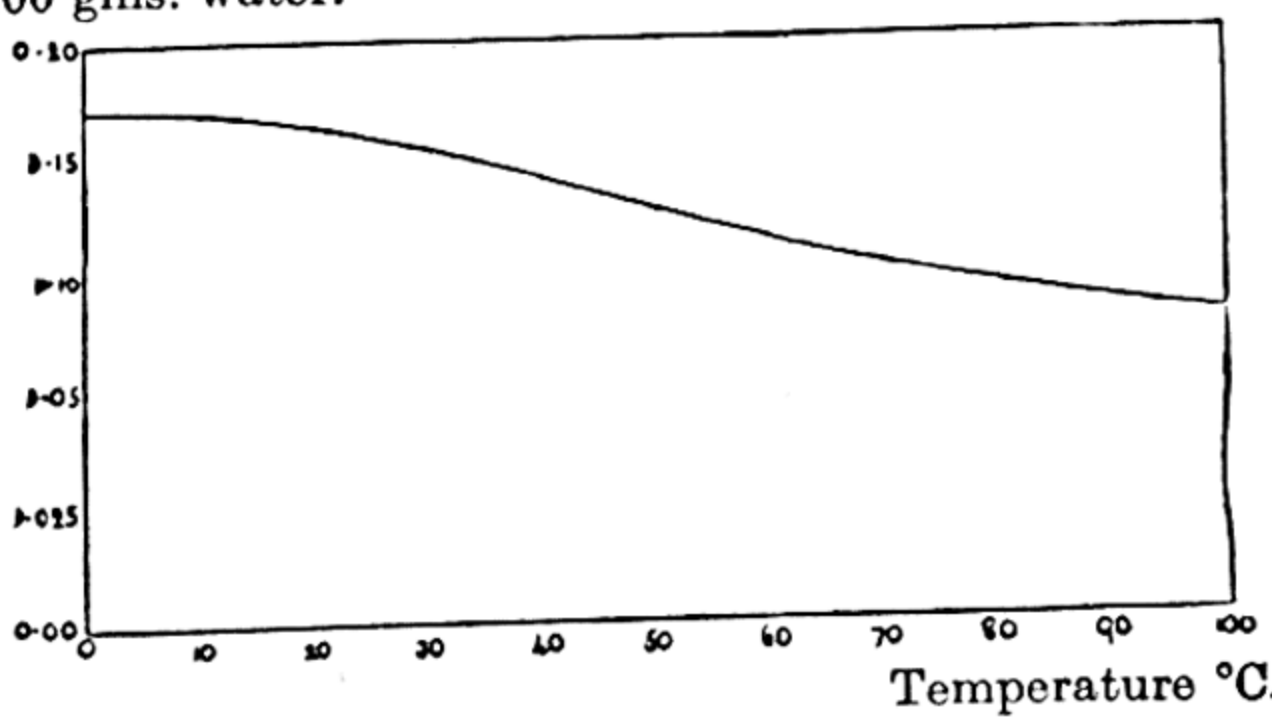



FIG. 24.—Solubility of Calcium hydroxide.

Concentration.
Gms. Chlorine per 100 gms. water.

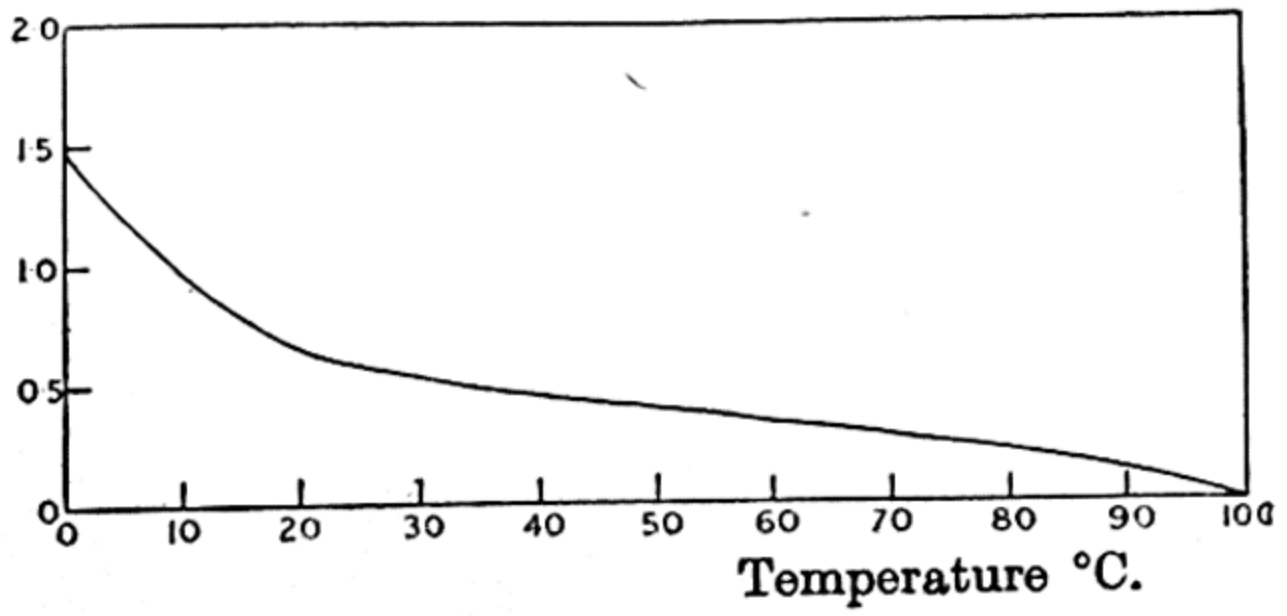



FIG. 25.—Solubility of Chlorine.

Where the solvent and solute form compounds, as in the case of many salts and water, each compound has its own solubility curve. As two compounds of this kind can only coexist in presence of the solution (§ 87) at one single temperature, these curves meet but do not intersect. Thus in Fig. 23 (DBC) we have the solubility curve of calcium chloride. The portion of the curve DB represents the solubility of calcium chloride hexahydrate $CaCl_2.6H_2O$, the portion BC the solubility curve of calcium chloride tetrahydrate $CaCl_2.4H_2O$. At the point B (29·5° C.) the hexahydrate, the tetrahydrate and solution can all remain in contact without change.

Many liquids are mutally soluble to a smaller or greater extent.

Thus, if bromine be shaken with water the water dissolves some bromine and the bromine some water, two saturated solutions being formed, called conjugate solutions. As the temperature rises the bromine dissolves more water and the water more bromine. The types of curve characteristic of the above case are not given here, as partial miscibility is not often met with in the study of inorganic chemistry.

Gases show a solubility curve such as that of Fig. 25. The solubility always diminishes with the temperature, and the form of the curve is always similar.

It is thus possible to remove almost all gases from their solutions by boiling, the only exceptions among the substances which are gases at normal temperature and pressure being the hydrogen halides (Chapter XXII.).

The solubility of gases is much influenced by pressure. The influence of pressure is in most cases regular and is summed up in Henry's law, which states that :

**The concentration of the solution formed by dissolving a gas in water is proportional to the pressure of the gas.**

Thus, if 100 gms. of water dissolve 0·0025 gm. nitrogen at atmospheric pressure, they will dissolve 0·01 gm. under four atmospheres pressure.

Henry's law is only obeyed by the part of the gas which dissolves without chemical change. It is therefore not obeyed by such gases as dissociate when they dissolve in water. Thus, let us suppose that in 1 volume of water at N.T.P. 1 volume of gas dissolves and that half of this dissociates to ions. Then 1 volume of water contains 0·5 volume unchanged gas and 0·5 volume in the form of ions. Let the pressure be doubled, $2 \times 0{\cdot}5$, *i.e.*, 1·0 volume of unchanged gas will be finally dissolved. This will not, as before, be in equilibrium with 1·0 volume of gas as ions, but with somewhat less, for dissociation is less complete in strong solutions.

Consequently, only (say) 0·9 volume of gas will be ionised in

the stronger solution. Thus doubling the pressure increases the solubility only from 1·0 to 1·9, not as Henry's law would predict, from 1·0 to 2·0.

If a compound of one molecule of gas and one or more molecules of solvent is formed, Henry's law will still apparently be obeyed, unless the concentration of gas is very high, for if we consider the concentration of the water to be unaffected by the dissolving of the gas, the law of Mass Action indicates that the proportion of dissolved free gas to dissolved combined gas will be constant. Thus carbon dioxide which forms the compound $H_2CO_3$, which is only to the minutest extent dissociated, appears to obey Henry's law : ammonia, which forms the more easily dissociated $NH_4OH$, does not.

**82. Methods of Making Solutions.**—Solutions can be made by merely bringing the solute and solvent into contact and leaving them until equilibrium is attained. In order to make a solution *quickly*, it is, however, desirable (*a*) to increase the surface of the solid as much as possible, *i.e.*, to *powder* it finely ; (*b*) to remove the saturated solution in the immediate neighbourhood of the particles of solid and so bring fresh unsaturated solution to act on them. This we do by *stirring* the liquid ; (*c*) substances in general dissolve more rapidly and to a greater extent at higher temperatures, and accordingly we *heat* the mixture of solid and liquid.

**83. Separation of the Solute and Solvent. Evaporation.**—In order to separate the components of a solution we use two physical methods:

(1) Evaporation and distillation.

(2) Fractional crystallisation.

*Evaporation.*—If a solution consists of a non-volatile solid or liquid dissolved in a volatile liquid, the solute may be recovered by allowing the solvent to evaporate. This process may be carried on at room temperature but is more usually performed at higher temperatures, at which evaporation is more rapid. If the substance is decomposed by gentle heat the former course is necessary, and since evaporation of aqueous solutions at room temperature is very slow, the process is often hastened by the use of the *vacuum desiccator* (Fig. 26). The water evaporates, and the vapour being carried off by a pump or absorbed in sulphuric acid, remains at a pressure much below the vapour pressure of water, and evaporation proceeds much more rapidly than in the open air.

FIG. 26.—Vacuum Desiccator.

If the solute is unaffected by heat the solvent may be simply boiled off. On the commercial scale ingenious multiple evaporators (§ 248) are used in order to economise heat. In these the steam evolved from a boiling solution is used to boil a second solution kept at a lower pressure, and therefore boiling at a lower temperature; the steam from this boils another solution at a still lower pressure, thus utilising the available heat in the most economical manner.

**84. Distillation.**—If the solvent is to be recovered from a solution, or if both solvent and solute are volatile and both are to be recovered, the process of distillation is used. If the solvent alone is volatile, simple distillation suffices to separate the solvent in a fairly pure condition. Traces of solute are, however, mechanically carried over as spray, and if the solvent is required in a very pure state one or more redistillations will be needed.

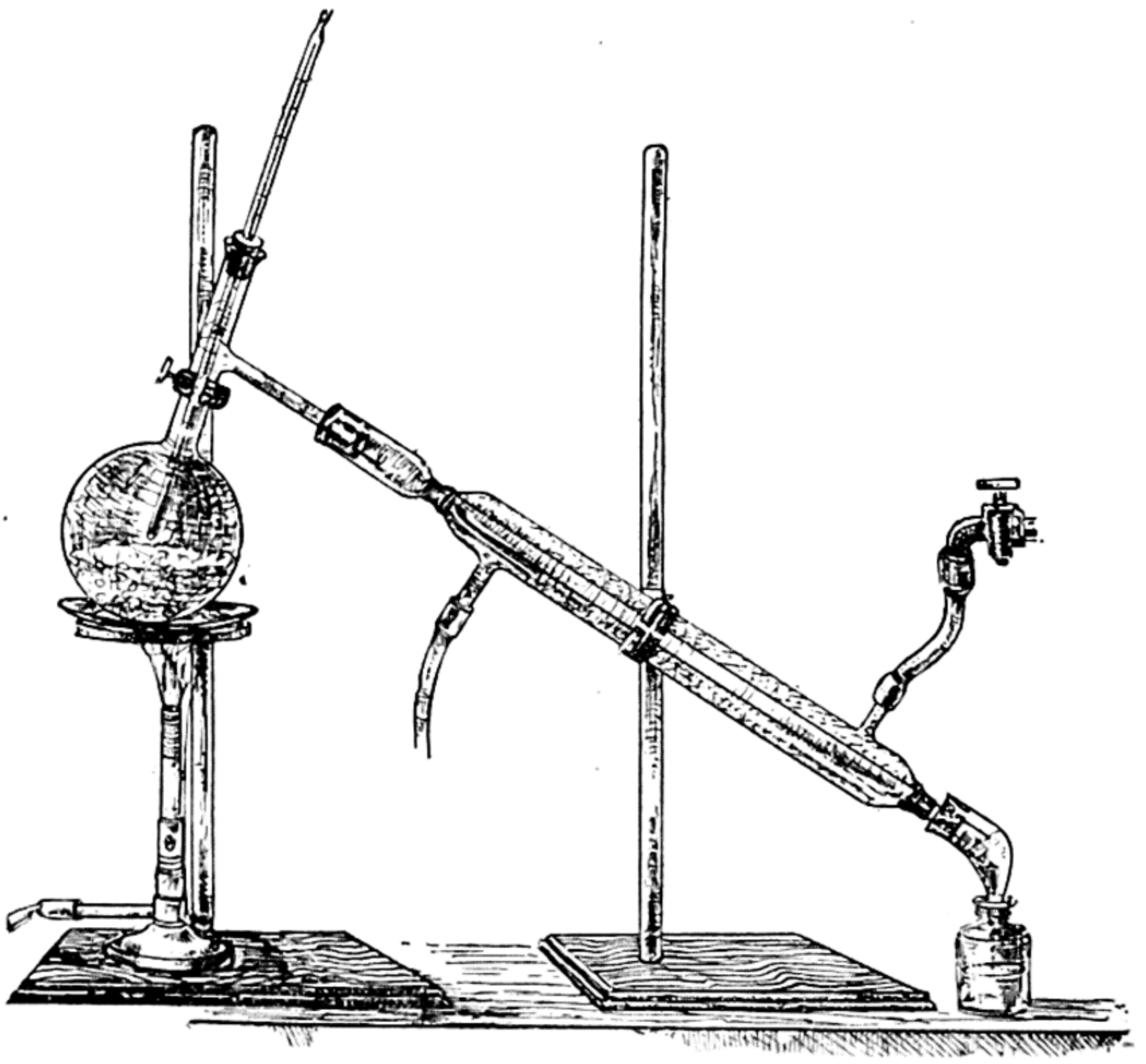


FIG. 27.—Simple distillation.

If the solution is a mixture of two volatile liquids with boiling points less than, say, 70–100° C. apart, fractional distillation is required to effect a satisfactory separation. Suppose the mixture to consist of a more volatile liquid, A, and a less volatile liquid, B. When such a mixture is heated each of these liquids gives off its

vapour and the vapour formed will contain *a greater proportion of A and a less proportion of B than the liquid.* The liquid distilling over will be richer in A and the liquid left in the flask will be richer in B than was the original liquid. Thus simple distillation can only afford a *partial separation* of two volatile liquids.

A device, known as the fractionating column or rectifier, is used in these cases. A fractionating column (Figs. 28, 29) consists of a vertical tube so arranged that some of the vapour condenses in it and runs back into the vessel where the liquid is being heated. The tube is so constructed that the vapour rising in the tube is brought into thorough contact with this condensed liquid. The vapour consists of the vapours of the more volatile A and the less volatile B. The latter will condense to a greater extent than the former and a film of liquid rich in B forms on the walls of the tube and runs down. The rising vapour heats this and in doing so evaporates more A than B from the film of liquid, but condenses more of its own B vapour in so doing. Thus the rising vapour condenses out B in the fractionating column and

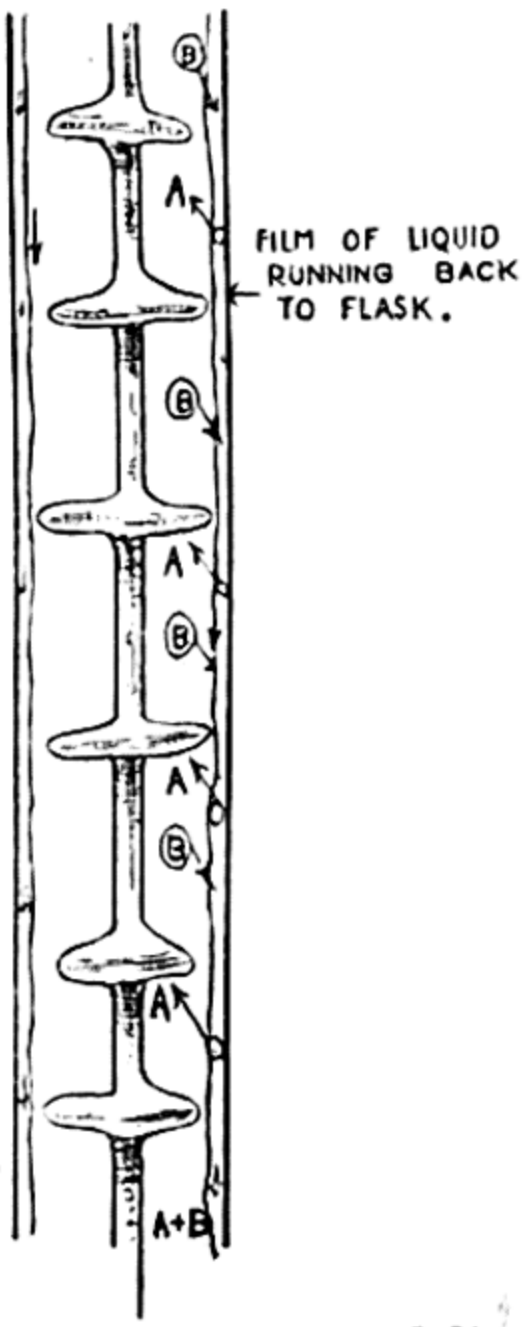



FIG. 28.—Rod and disc fractionating column in action.

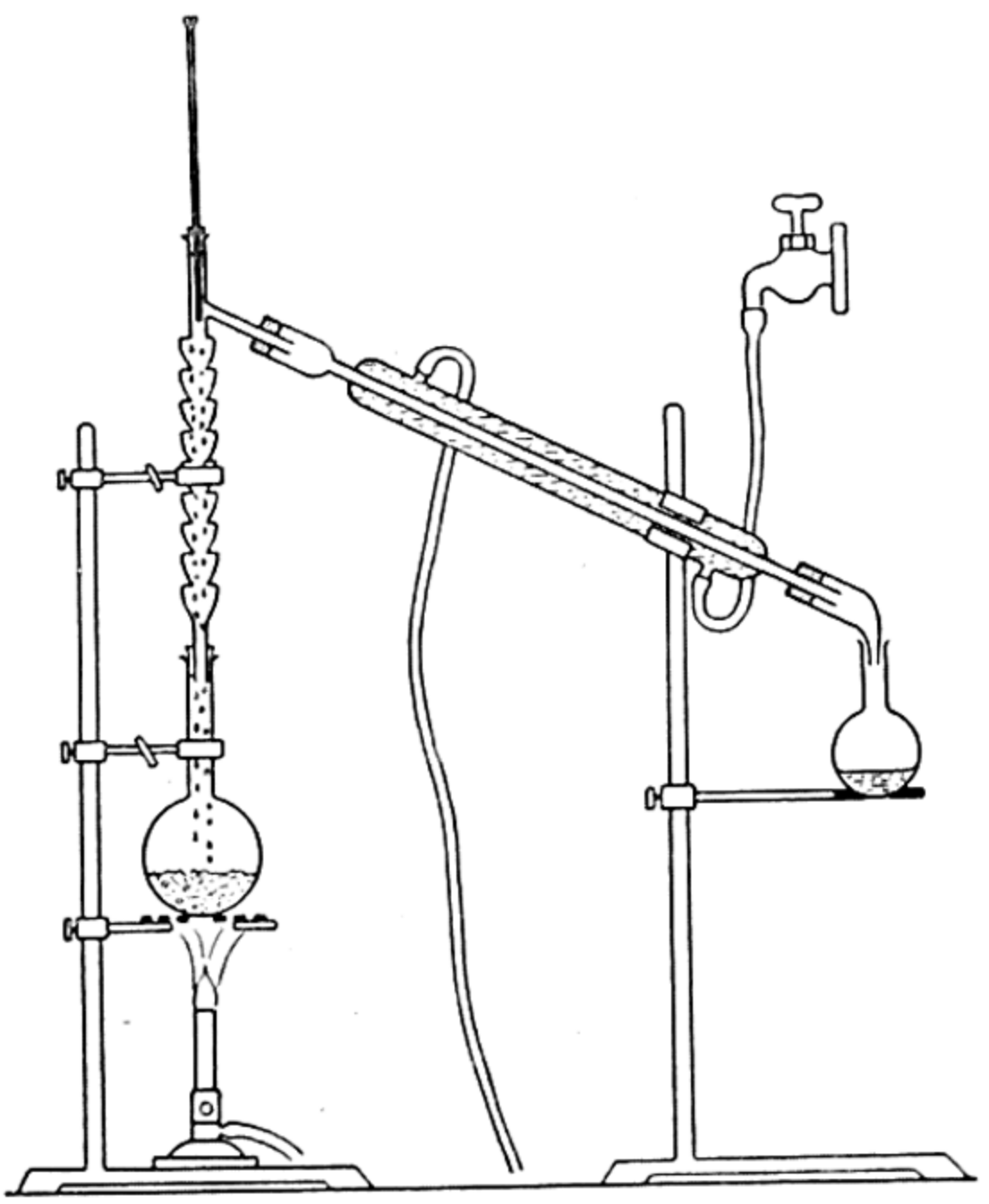


FIG. 29.—Fractional distillation using "pear" column.

takes up A, and so, as it rises, becomes steadily richer in the more volatile material. In this way an almost complete separation may be attained in one distillation if the boiling points of the two liquids lie more than about 30° C. apart. If the difference is less than this, several successive fractionations will be found necessary.[1]

[1] The efficacy of the process does not really depend on the difference of boiling points, but on the difference of vapour pressure at the temperature of condensation. The difference of boiling point affords a rough indication of this difference of vapour pressure.

Various patterns of fractionating column are used. In the laboratory the "pear" column is efficient and strong and is probably the most often used. The rod-and-disc form is illustrated in Fig. 28, and is also efficient though less well-adapted for rapid distillation. On the commercial scale large *rectifiers* are used, consisting of towers in which the vapour is forced through successive shallow layers of the condensed liquid.

The separation of a solid from a solution is brought about not only by processes of evaporation but also by cooling the solution until it becomes saturated and the solid separates.

**85. Separation of Mixtures by Crystallisation.**—Two soluble substances may be readily separated by crystallisation (*a*) if their solubilities are widely different, or (*b*) if they are present in very different quantities.

Suppose, for example, we have a mixture of equal parts of sodium nitrate and potassium nitrate, the solubilities of which are 88·11 and 33·02 gms. per 100 gms. water, respectively, at 20° C.

If we assume that the solubility of each salt is not affected by the presence of the other (an assumption which is only an approximation to the truth) it will be seen that if we dissolve 100 gms. of the mixture in 100 gms. of hot water and allow the liquid to cool, only potassium nitrate will crystallise out, for the solution, even when cold, will not be saturated with sodium nitrate (50 gms. per 100 c.c.). It is not possible by this method to separate the more soluble salt in a pure condition.

If, however, only a small proportion of the salt is present as an impurity in another it is usually possible to remove this even if it is less soluble than the salt which it is required to separate in a state of purity.

Thus, suppose some hydrated sodium carbonate contains 1 per cent. of sodium chloride. If 150 gms. of this are dissolved in 100 gms. of water by heating, the solution will contain only 1·5 gms. of sodium chloride, and consequently will not be saturated with this salt. The sodium carbonate will crystallise on cooling and the crystal will be free from sodium chloride, except in so far as the latter salt is entangled in the crystals as adherent mother-liquor, etc.

Where two salts form *mixed crystals*, that is to say, when each crystal of the solid separating contains both salts, then it is impossible to separate the salts by a single crystallisation, and the process of fractional crystallisation must be adopted.

**86. Fractional Crystallisation.**—The separation by crystallisation of two substances which are of markedly different solubility is readily performed; but if the substances to be separated differ only slightly in their solubility or form mixed crystals, the slow process of fractional crystallisation must be adopted. In separating the compounds of two very similar elements, *e.g.*,

barium and radium compounds or hafnium and zirconium compounds, fractional crystallisation is often the only means at our disposal.

Let us suppose we have a mixture containing two substances, A and B, present in about equal quantities; and let us suppose that they are of about the same solubility but that A is rather less soluble than B. The mixture is dissolved in water, the solution being made up of such a strength that, on cooling, a part, say half, of the solid crystallises out. This part will contain less of the more soluble salt B and more of the less soluble salt A than the original mixture, while the mother-liquor contains more of B and less of A. The solid product richer in A is then again crystallised as before and a material still richer in A is obtained. The mother-liquor left from the first crystallisation is evaporated and again crystallised, and a B-rich liquid and A-rich solid are obtained from this. Thus each set of crystals and each mother-liquor are repeatedly separated into A-rich and B-rich portions and the final results are specimens of A and B containing but little of the other constituent.

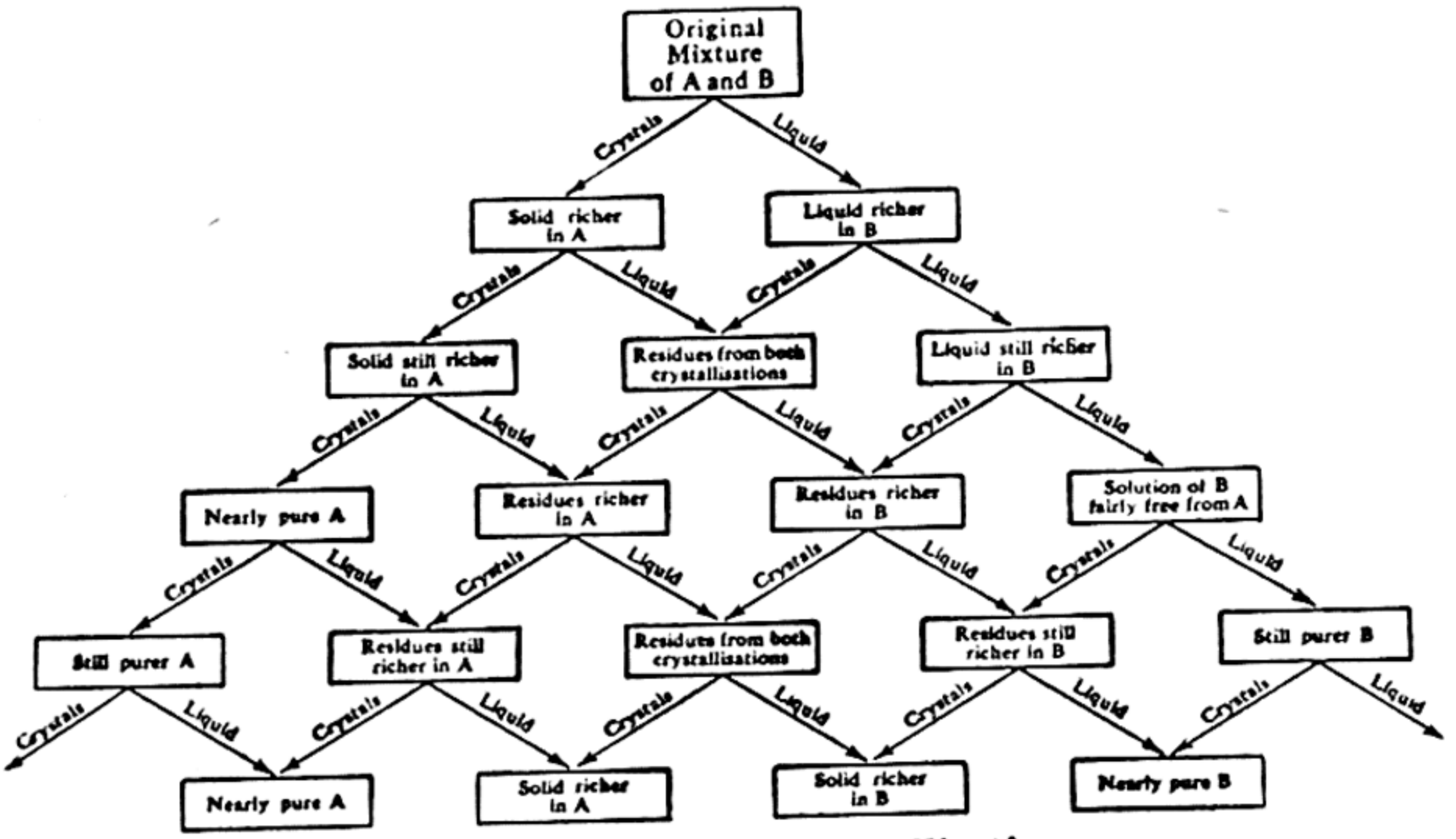



FIG. 30.—Fractional crystallisation.

**87. The Phase Rule.**—Our most useful guide in studying solubilities and many other phenomena is the Phase Rule, and the student should master its simple terminology.

The Phase Rule deals with the behaviour of heterogeneous systems at equilibrium. A heterogeneous system is one made up of different portions, each in itself homogeneous but separated from the others by bounding surfaces. Each of these portions is called a *Phase*.

Thus, in a mixture of ice and water enclosed in an evacuated flask there are three *phases*—ice, water, and water vapour, separated from each other by surfaces. In a saturated solution of copper sulphate in contact with the solid there are three phases—hydrated copper sulphate, solution and vapour. A solution of salt is only one phase, for no bounding surface marks off the salt from the water.

Again, suppose some calcium carbonate is heated in a closed vessel to 800° C. The substance will partially decompose and three phases will be present—calcium carbonate, calcium oxide, and carbon dioxide.

The notion of *components* is a little harder to grasp.

As *components* of a system are to be chosen the smallest number of independently variable constituents by means of which the composition of each phase can be expressed in the form of a chemical formula or equation.

Thus in the case of the water-ice-vapour system only one component is required—water ; for the formula of each phase is $H_2O$.

In the case of copper sulphate in contact with its solution we require two components—copper sulphate $CuSO_4$ and water $H_2O$. The phases are

Water vapour = $H_2O$.
Solution = $nCuSO_4 + mH_2O$.
Solid = $CuSO_4 . 5H_2O$.

In the case of calcium carbonate we may take calcium oxide and carbon dioxide as components for—

Calcium carbonate = $CaO + CO_2$.
Calcium oxide = $CaO$.
Carbon dioxide = $CO_2$.

We do not choose calcium, carbon and oxygen for they are not independently variable and we do not need as many as three.

*Degrees of Freedom.*—The number of degrees of freedom of a system is equal to the number of independently variable factors (temperature, pressure, and concentration of each component), which have to be fixed before the state of the system is completely defined.

Thus, before we can define the state of the system consisting of copper sulphate crystals in contact with their solution, we must fix one factor, *e.g.*, the temperature, for the strength of the solution is dependent on this. If we fix the temperature the system is then defined, for to each temperature corresponds a definite concentration of the saturated solution and a definite vapour pressure. If we fix the vapour pressure or the strength of the solution we shall also find once more that the solid, solution and vapour can only coexist under one set of conditions. We say then that this system has one degree of freedom, *i.e.*, is *univariant.*

The Phase Rule states that:

*The number of phases present at one time in a system at equilibrium, together with the number of degrees of freedom, is equal to the number of components increased by two.* This is stated in the formula.

$$P + F = C + 2.$$

This rule is found, experimentally, to be true, but it can also be derived by arguments of which the following is a simple outline. In any given equation the degrees of freedom, or possible choices, is given by the difference between the number of unknown and known quantities. Thus in the equation : $x + y = 3$, we have one degree of freedom ; give $x$ any value, and the magnitude of $y$ is fixed, for we have two unknowns, $x$ and $y$, and one known, the equation itself.

In specifying the conditions of heterogeneous equilibrium in a system of P phases consisting of C components we have the following unknowns: P, C concentrations, temperature, and pressure, that is, P + C + 2.

The number of " knowns " consist of P phase equations ($P . V = R . T$ is a phase equation, that of the gaseous state), and $C(P - 1)$ interphase equations,

representing the conditions of equilibrium between two phases (the distribution law, $c'/c = k$, is an example of an interphase equation).

Now the degrees of freedom, F = (Number of unknowns) − (Number of knowns).

That is,
$$F = P \,.\, C + 2 - P - C(P - 1)$$
$$F = C - P + 2$$
or,
$$P + F = C + 2$$

Let us consider the case of a salt and water. We may take sodium sulphate as an example. This salt forms only one stable hydrate,[1] $Na_2SO_4 \,.\, 10H_2O$.

The possible stable phases are :

| | |
|---|---|
| Anhydrous sodium sulphate . . | $Na_2SO_4$ |
| Hydrated sodium sulphate . . | $Na_2SO_4 \,.\, 10H_2O$ |
| Sodium sulphate solution . . | $nNa_2SO_4 + mH_2O$ |
| Ice . . . . . | $H_2O$ |
| Water vapour . . . . | $H_2O$ |

There are thus five phases and two components, for the components $Na_2SO_4$ and $H_2O$ are enough to express the composition of all these phases. According to the Phase Rule, then,
$$P + F = 2 + 2,$$
and it follows that

(*a*) with one phase only present the system is tervariant (F = 3)

(*b*) with two phases present the system is bivariant (F = 2) ;

(*c*) with three phases present the system is univariant F = 1).

(*d*) with four phases present the system is invariant (F = 0) ;

(*e*) five phases cannot coexist.

*Case* (*a*) hardly interests us. If we have, for example, a bottle containing sodium sulphate solution we have to specify the temperature, the pressure upon it and the concentration (three factors) before we know all about it.

*Case* (*b*).—A solution of sodium sulphate in contact with the solid hydrate. By fixing temperature, and pressure (which slightly alters solubility) we know the concentration, and thus all about the system.

*Case* (*c*).—The most important cases where three phases are present are those when ice, solution and vapour are in equilibrium; and when sodium sulphate (decahydrate or anhydrous) its solution and water vapour are in equilibrium. In these cases the system is univariant, and if we fix one factor—say, temperature—the other factors, vapour pressure and concentration, are therefore also fixed.

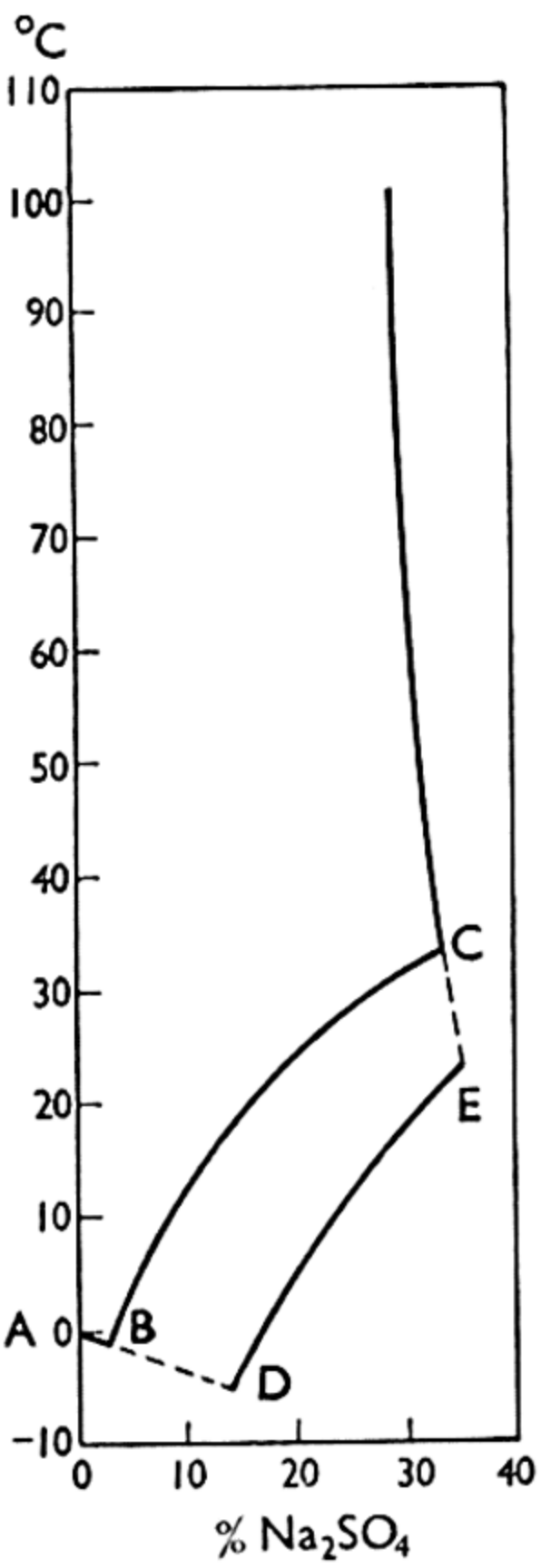



FIG. 31.—Sodium Sulphate Solubility curves.

*To each temperature corresponds a particular concentration of the solution* and a *line* (the solubility curve) on the solubility diagram therefore represents these

[1] There is an unstable heptahydrate $Na_2SO_4 \,.\, 7H_2O$.

equilibria. The diagram (Fig. 31) contains three lines and each represents a different equilibrium. Starting at the left of the diagram, if we cool a solution of sodium sulphate (say of 2 per cent. strength) ice will separate out and the solution will accordingly become stronger and freeze at a lower temperature. Further cooling will freeze out more ice and finally at — 1·2° C. the curve showing the concentrations and temperatures at which *ice* and sodium suphate solution and vapour are at equilibrium meets the curve BC, showing the concentrations and temperature at which sodium sulphate decahydrate, solution and vapour are in equilibrium. At this point (B), therefore, vapour, solution, ice and sodium sulphate solution are all in equilibrium (*v.* (*d*), below).

If a solution containing more than 3·85 per cent. of sodium sulphate, say 17 per cent., is cooled, at a certain temperature (20° C.) sodium sulphate decahydrate crystallises out and the solution becomes weaker. Further cooling causes more crystallisation and the saturated solution finally reaches the temperature and concentration shown by the point B (3·85 per cent.), when ice also freezes out and the whole solution solidifies without change of temperature. No solution containing sodium sulphate will yield the anhydrous salt when cooled, but a solution of concentration 33 per cent. will yield this phase when heated, and any solution of temperature greater than 32·5° C. will yield it when *evaporated*. Thus a solution containing 10 per cent. sodium sulphate if evaporated at 80° C. will deposit the anhydrous salt when its concentrations reaches 30·2 per cent.

Again, if a mixture of sodium sulphate decahydrate and solution is heated the solution will become stronger until a temperature of 32·5° C. is reached (C). The anhydrous salt then begins to be formed and the four phases, anhydrous salt, hydrated salt, solution and vapour, are all present. The temperature then remains constant although heat is being supplied. The decahydrate decomposes, and as soon as it has all gone and three phases, anhydrous salt, solution and vapour, only remain, the temperature rises, the anhydrous salt depositing, and the solution becoming weaker.

*Case* (*d*).—There are only two *points* on the diagram when four phases can coexist, *i.e.*,

B. — 1·2° C. 3·85 per cent. gms. sodium sulphate per 100 gms. water. { ice. / decahydrate. / solution. / vapour.

C. 32·5° C. 33·2 gms. sodium sulphate per 100 gms. water. { sodium sulphate decahydrate. / anhydrous sodium sulphate. / solution. / vapour.

At these points there are four phases and so

$$F + 4 = 4,$$

*i.e.*, no factors have to be fixed before the state of the system is fixed. *Thus, when four phases are present temperature and pressure and concentration are all fixed.*

These points are, therefore, useful from the point of view of thermometry. Point B is the eutectic (*v.* § 88) and Point C is a transition-point. Any solution of sodium sulphate, if cooled, will finally come to the eutectic temperature and there remain till freezing is complete.

Unstable Phase.—There exists a hydrate of sodium sulphate, $Na_2SO_4.7H_2O$,

which can exist only in contact with solutions stronger than those which would be in equilibrium with the decahydrate at the same temperature. It is therefore unstable, and either spontaneously or on addition of a crystal of the decahydrate, the latter crystallises out and the heptahydrate re-dissolves. Its solubility curve is represented by DE (Fig. 31).

**88. Freezing Mixtures.**—The eutectic point of a solution is the only point at which ice, water-vapour, solid and solution, can all four be in equilibrium. If we mix a solid salt with ice the salt and the moisture on the ice will form a solution. Ice will be in equilibrium with this solution only at some lower temperature, and it melts, withdrawing the necessary latent heat from the mixture. The temperature falls and equilibrium is only reached when ice, salt, vapour and solution can all coexist permanently, *i.e.*, at the eutectic point. This point varies considerably for different substances. For barium nitrate it is only – 0·7° C., for common salt it is – 21·2° C., while for crystallised calcium chloride it is – 51° C. These are the temperatures which will be reached by suitable mixtures of ice and the salts. It is not easy to make up freezing mixtures to reach such very low temperatures as that corresponding to the eutectic point of calcium chloride, for the leakage of heat from the walls of the containing vessel, etc., causes so much ice to melt that the solid salt is apt to become completely dissolved, giving a less concentrated solution than that which is in equilibrium with ice at the eutectic point.

Among the best freezing mixtures are the following mixtures of ice and salts.

| Soluble Substance. | Weight of Soluble Substance. | Weight of Crushed Ice or Snow. | Lowest Temperature Reached. |
|---|---|---|---|
| Calcium chloride hexahydrate $CaCl_2.6H_2O$ . . . | 100 | 70 | – 51° C. |
| Common salt, NaCl . . | 33 | 100 | – 21·2° C. |
| 66 per cent. sulphuric acid . | 100 | 110 | – 37° C. |

Another type of freezing mixture dispenses with ice and depends on the negative heat of solution of certain salts. Thus the mixture of 100 parts of ammonium nitrate with 130 parts of water falls in temperature by about 27° C.

**89. Solutions containing more than One Salt.**—It is usually impossible to predict with exactness the quantities of *two* substances which can be dissolved in the same portion of liquid. As a general rule substances other than acids, bases and salts affect each other's

solubility only to a small extent. Thus, in general, if $n$ grams of a substance A can be dissolved in 100 gms. of water and $m$ grams of a substance B can be dissolved in 100 gms. of water, then a solution saturated with both A and B will, as a rule, contain but slightly less than $n$ grams of the former and $m$ grams of the latter.

Two salts, however, which do not yield a common ion will dissolve to a greater extent when dissolved together than when dissolved separately.

If the salts yield a common ion (as two nitrates, two sulphates, two sodium salts, etc.) they diminish each other's solubility (§ 118).

**90. Double Salts.**—The formation of double salts, loose compounds of two or more simple salts is very common. Examples of such salts are the alums (§ 493), ferrous ammonium sulphate (p. 769), cupric potassium chloride, etc. ($CuCl_2.2KCl.2H_2O$). The conditions of solubility of these can be studied with the aid of the Phase Rule, but is beyond the scope of this book.

*Preparation of Double Salts.*—As a rule, double salts can be made by mixing concentrated solutions of the single salts in the proportions required by the formula.

Thus ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$, may be made by mixing warm concentrated solutions of ferrous sulphate and of ammonium sulphate and allowing the mixture to cool.

Many double salts can exist only under certain conditions of temperature. Thus *Astracanite*, $Na_2SO_4 . MgSO_4 . 4H_2O$ can only exist above 22° C., while cupric potassium chloride only exists below 92° C.

Again, many double salts can only exist in presence of a concentrated solution of one constituent. The double iodide of potassium and lead can only be made by using an excess of concentrated potassium iodide solution. The addition of water at once decomposes it into potassium iodide and lead iodide.

When a double salt is brought into contact with water it ordinarily dissolves, forming a solution which has the properties of both the salts of which it was composed. A solution of alum, for example, is indistinguishable from a mixture of the solutions of aluminium sulphate and of potassium sulphate (but see § 171).

**91. Colloidal Solutions.**—Many substances which normally appear to be insoluble in water can be converted into *colloidal* solutions which differ from ordinary solutions in many respects. Thus, arsenic sulphide is, as ordinarily made, insoluble in water, but if a solution of hydrogen sulphide is poured into a dilute solution of arsenic trioxide the arsenic sulphide remains in solution. Again, gold is insoluble in water, but by careful reduction of solutions of gold chloride brightly coloured solutions of metallic gold are obtained.

These 'colloidal solutions' are intermediate in character be-

tween ordinary solutions and mere suspensions, resembling the latter, perhaps, the more closely, and it has been shown that they are either solutions of solutes of very high molecular weight ($> 800$) or suspensions of exceedingly fine particles, each consisting of many molecules.

There is, however, no sharp distinction between colloidal and ordinary solutions, every stage of transition being found among solutions of substances of fairly high molecular weight.

**92. Preparation of Colloidal Solutions.**—Since most colloidal solutions are unstable in presence of electrolytes—acids, alkalis and salts—it is essential in preparing them to use materials of high purity and very clean apparatus.

The chief methods of making colloidal solutions are :—

(1) *By Chemical Precipitation.*—If a very insoluble material is precipitated from dilute solution in absence of any considerable quantity of ions, a colloidal solution is often formed. Thus, if a cold dilute neutral solution of arsenic trioxide is saturated

$$3H_2S + As_2O_3 = As_2S_3 + 3H_2O$$

with hydrogen sulphide and filtered from coarser particles a clear yellow colloidal solution of arsenic sulphide is obtained.

Again, if very dilute solutions of salts of the noble metals, say, gold chloride or silver nitrate, are reduced by certain substances, *e.g.*, hydroxylamine, phosphorus dissolved in ether, formaldehyde, etc., the resulting metal is not precipitated but remains suspended as a strongly-coloured colloidal solution.

(2) *By Mechanical Dispersion.*—Mere fine grinding may be enough to bring a solid into colloidal solution. India ink forms a rather coarse colloidal solution and is simply made by grinding lamp-black with water and adding a little gum.

Bredig's electrical method consists of causing an arc to pass between thick wires of silver, gold or platinum immersed in pure iced water. The minute particles resulting from the condensation of metallic vapour and the mechanical disruption of the electrodes form a colloidal solution.

**93. Optical Properties of Colloidal Solutions.**—Colloidal solutions are distinguished by remarkable optical properties not possessed by ordinary solutions. In the first place, they are not optically homogeneous. A beam of light passed through such a solution shows a visible luminous track, while such a beam passing through pure water or a true solution is invisible. The light emitted by the luminous track is polarised. These properties indicate the presence in the solution of particles large enough to scatter the light passing through it. On examination with even a first-rate microscope most colloidal solutions, however, show no particles whatever and, accordingly, the particles of, say, colloidal gold are less than about ·0004 mm. in diameter.

The actual presence of the particles and their size can be determined by the use of the ultramicroscope, which consists of a powerful microscope focused upon a cell containing the colloidal solution.

Through this cell is passed an intense beam of light at right angles to the optical axis of the microscope. The beam itself does not enter the lens, and the field would remain dark were it not that the colloid particles scatter the light and appear as bright points of light in rapid motion. The size of these points of light is very much greater than that of the particles which cause them.

The actual size of the particles has been determined by counting the particles in a minute but known quantity of the solution by means of the ultramicroscope, and then determining the weight of the particles in a large quantity of the same solution.

Thus, in a certain experiment, 0·01 c.c. of a solution of colloidal silver which had previously been diluted 100 times, contained 300 particles of silver.

Of the original solution 100 c.c. contained 0·0068 gm. silver.

Then ·0001 c.c. contained $\frac{\cdot 0068 \times \cdot 0001}{100}$ gm. silver.

and one particle contained $\frac{\cdot 0068 \times \cdot 0001}{100 \times 300}$ gm. silver.

$$= 2{\cdot}3 \times 10^{-11} \text{ gm.}^1$$

The density of silver is 10·5 and the volume of each particle was $\frac{2{\cdot}3}{10{\cdot}5} \times 10^{-11}$ c.c.

and, assuming them to be spherical, their radius was given by

$$\tfrac{4}{3}\pi r^3 = \frac{2{\cdot}3 \times 10^{-11}}{10{\cdot}5} \text{ cm.}$$

$\therefore$ the diameter $= 1{\cdot}611 \times 10^{-4}$ cm.

Colloidal solutions pass through most filters unchanged, but *ultrafilters* prepared by treating filterpapers with collodion will retain the particles.

**94. The Brownian Movement.**—If very fine particles of any insoluble solid are suspended in water, they remain permanently in a state of ceaseless motion. The motion can be observed with particles visible under the microscope—a drop of diluted india ink shows it well under a power of about 1,000 diameters. The motion is irregular and depends only on the size of the particles, the temperature and the viscosity of the liquid.

Small particles show more rapid motion than large ones and the minute particles of colloidal gold are in very vigorous motion indeed. The Brownian movement is due to the repeated blows directed by the ceaselessly moving molecules of the liquid upon the suspended particles. A particle of carbon in india ink, at one particular moment, may be struck by half a dozen more molecules on the left side than on the right ; it is thus shifted to the right, while a fraction of a second later the process may be reversed and it may be

[1] The weight of a silver atom is about $1{\cdot}7 \times 10^{-22}$ gm. so that even these minute particles would contain more than $10^{11}$ atoms each.

shifted to the left or up or down. The motion is quite irregular, and Einstein based on this fact a calculation relating to the total distance travelled in a given time, and from this distance it has been found possible to calculate the number of molecules in a gram-molecule of a compound (the Avogadro N, § 137).

**95. Electrical Properties of Colloidal Solutions.**—Colloidal solutions are remarkable in that their particles are electrically charged, in some cases positively, in others negatively. Thus, if they are subjected to the action of an electric current the particles wander slowly to one pole or the other. They are precipitated by the addition of charged particles in the form of ions. Ions bearing a single charge are the least effective, and the precipitating power increases very rapidly with the number of charges. Thus aluminium salts yielding the ion $Al^{+++}$ are about a thousand times as effective, weight for weight, as potassium salts yielding the ion $K^{+}$. The use of alum in precipitating sewage and in tanning hides depends on this property.

**96. The Two Classes of Colloidal Solutions.**—Colloids fall definitely into two classes, the '*lyophobe*' colloids, which are represented by the fine suspensions we have mentioned above, and the '*lyophile*' colloids, which display a somewhat different set of properties.

Both sets of colloidal solutions display certain common properties, such as the scattering of a beam of light, the tendency for the dissolved substance to move under an electromotive force, precipitation by electrolytes, etc.

The lyophilic solutions include such solutions as those of starch, gelatine, silicic acid, etc. These differ in several respects from the metallic and other lyophobic sols we have hitherto considered. The chief distinction between colloidal solutions of the two types is that the lyophilic colloids may be recovered from solution by evaporation or precipitation, and the material so recovered may again be dissolved to form a colloidal solution. The lyophobe colloids, on the other hand, once precipitated from solution cannot be redissolved. Lyophilic colloids are also much more stable. Considerable quantities of electrolytes are needed to precipitate them and they will impart this insensitiveness to lyophobe colloids, such as colloidal silver. A mixture of the latter with, say, albumen, is very stable and may be preserved for long periods. The particles present in lyophilic colloidal solutions are, moreover, very much smaller than are those of the lyophobe colloids.

These lyophilic colloidal solutions are highly viscous as a rule, and they also have the remarkable property of setting to a jelly or *gel*.

**97. Gels.**—A strong colloidal solution usually sets to a jelly as a

result of cooling and by warming is again converted to a solution. Thus a solution of gelatine or soap, when cooled, forms a jelly, which on warming liquefies once more, and this process may be repeated any number of times. A jelly of this kind has a heterogeneous structure and may contain a honeycomb network of cells or filaments; or films of more solid material enclosing a less viscous liquid. Gels are also obtained by coagulation. Aluminium hydroxide or ferric hydroxide or silicic acid are precipitated as gels which differ from those of gelatine, etc., in that they will not liquefy on warming. These gels, when dried, retain water very obstinately, and it is impossible to dry them at, say, 100–110° C. to a constant composition. It is only by heating them to near a red heat that we can expel the water from them.

## The Crystalline State.

**98. Characteristics of Crystalline Substances.**—A solid homogeneous substance may be either crystalline or amorphous. Although in most cases the characteristic form which is the most striking property of a crystal does not emerge, it is found that the great majority of solid substances are built up of aggregates of large or small crystals, or have some of the properties associated with crystalline structure. Glasses, if we admit them as solids, are non-crystalline; but we should rather regard them as super-cooled liquids.

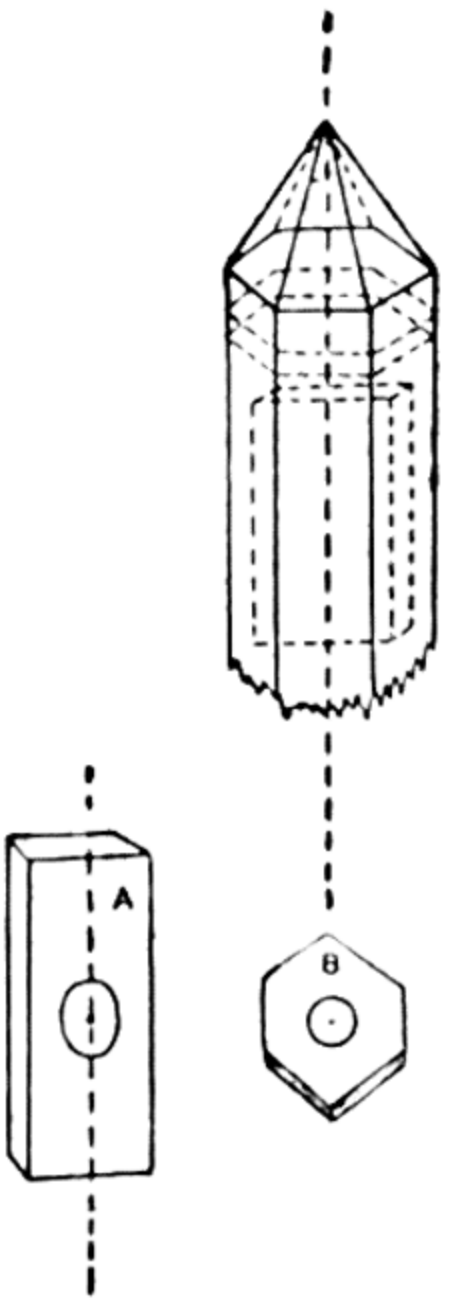



Fig. 32.—Showing that the conductivity of quartz varies according to the direction in which it is measured.

The essential properties of crystalline substances are two.

(1) They are anisotropic.

(2) They tend to assume a characteristic form.

(1) An *isotropic* substance is one of which the properties do not vary with the direction in which they are measured. Thus the refractive index, elasticity or conductivity of a sphere of glass is precisely the same if measured along any diameter. This is not the case with a sphere cut from a piece of rock-crystal. We say that glass is *isotropic* and rock-crystal is *anisotropic*.

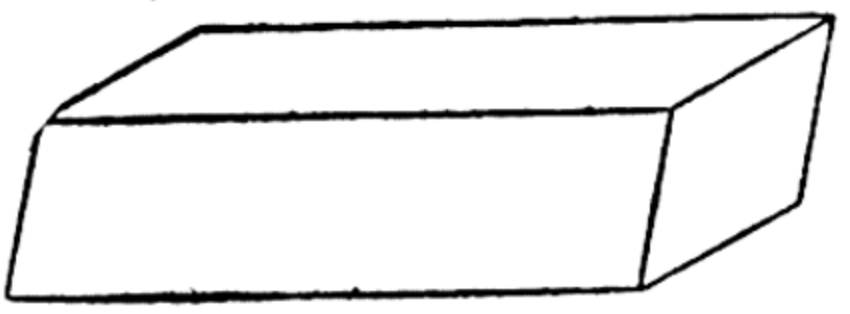
We find then that crystals in general are anisotropic, and such of their properties as are directional in character vary with the direction

relative to the axes of the crystal in which they are measured. Thus the conductivity of a crystal to heat or electricity varies with its direction. If plates cut from a quartz crystal in a direction parallel to its longitudinal axis, be coated with wax and heated by means of a hot wire applied at one point, the area of melted wax takes an elliptic form, showing that the heat is conducted more rapidly in the direction of the long axis of the crystal; a plate cut at right angles to the axis shows, however, no such asymmetry.

Other properties which may vary with the direction in the crystal along which they are measured are the colour, behaviour to polarised light, magnetic properties, elasticity, hardness and coefficient of linear expansion.

(2) Crystalline matter has a tendency to assume *a characteristic form* when deposited in such a manner as to allow of its development. The form assumed is always that of a polyhedron, a solid bounded by plane surfaces intersecting at straight edges. Such a form is the expression of an internal structure and the form assumed is characteristic of the substance crystallising.

The property of ' cleavage ' is also characteristic of crystals. The cohesion between the parts of the crystal is a minimum along certain planes. The molecules in a crystal are regularly arranged so that certain planes drawn through the crystals will pass through very many molecules, while other planes may be drawn so as to pass



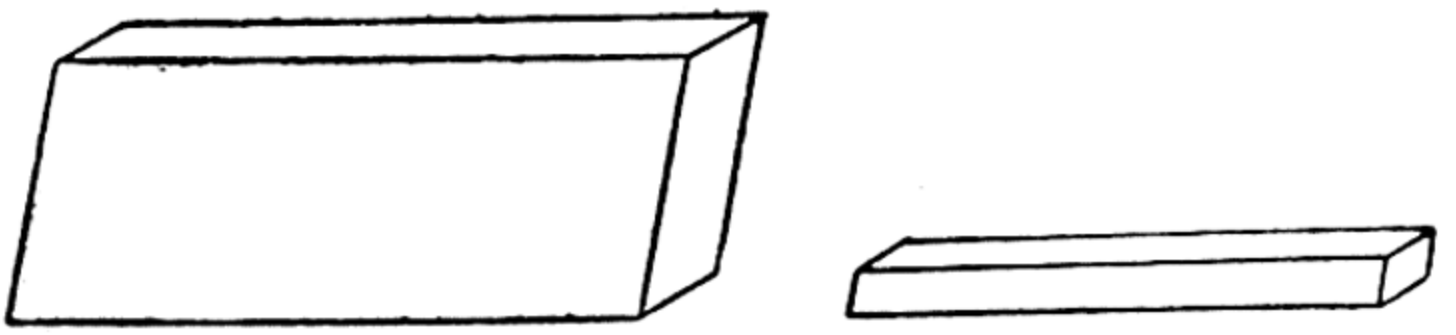


FIG. 33.—Cleavage fragments of calcite.

through few or none, and accordingly the crystal tends to split in such a way as to separate along these latter planes. This property is displayed by almost all crystals. The cleavage may be exhibited parallel to the faces of the original crystal, but this does not always occur. Calcite shows cleavage very clearly. Calcite crystals cleave along three planes ; other crystals, as, for example, diamond, along four ; others, as mica, along one only. A few crystals, such

Sri Pratap College.

| System. | Also known as | Axes of symmetry. |
|---|---|---|
| I. Cubic . . | *Regular, Octahedral.* | Three equal fourfold axes at right angles. |
| II. Tetragonal . | *Quadratic.* | Three axes, two equal, one unequal, at right angles. |
| III. Orthorhombic. | *Rhombic, Prismatic* | Three unequal axes at right angles to each other. |
| IV. Monoclinic . | *Oblique.* | One axis of symmetry and a plane of symmetry perpendicular to it. |
| V. Anorthic . | *Triclinic.* | No axis or plane of symmetry. A centre of symmetry may exist. |
| VI. Hexagonal . | — | One sixfold axis; three twofold axes at right angles to it. |
| VII. Rhombohedral | — | One three-fold axis: three twofold axes at right angles to it. |

as those of quartz, show no tendency to cleavage. The cleavage of diamonds is used as a means of cutting these intensely hard crystals.

**99. The Characteristic Forms of Crystals.**—The study of the form of crystals is a difficult task, and is in some respects geometrical rather than chemical in character.

The classification of crystals into systems is based on the degree of *symmetry* shown by the crystals, the cubic system having the highest degree of symmetry. Without some little knowledge of solid geometry it is not possible to appreciate the method of classification into seven systems and thirty-two types, and it must suffice here to give photographs of real crystals of each type. In studying the photographs of Plates IV.–X. it should be remembered that the *symmetry* and not the particular external form is the criterion of classification of a crystal. Thus a cube and a regular octahedron exhibit the same type of symmetry, and crystals which

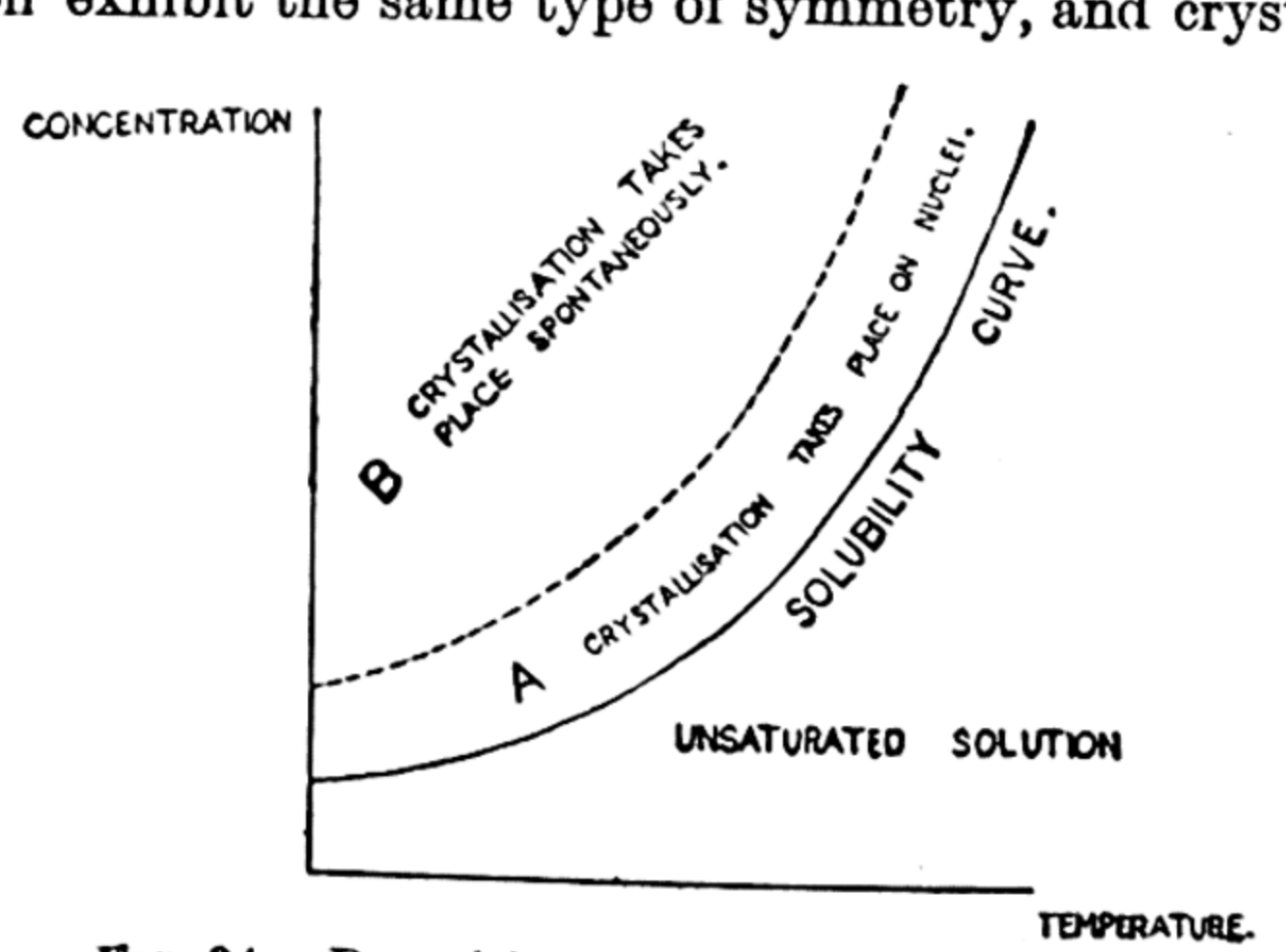



FIG. 34.—Deposition of crystals from solution.

are perfect octahedra may therefore belong to the *cubic* system.

**100. Deposition of Crystals from Solution.**—A solution of a substance is in equilibrium with the solid when it is saturated with it. If such a solution is ever so little cooled it will no longer be in equilibrium with the solid, and if any particles of the solid are present these will grow into crystals of the substance in question. If no such particle is present the question of equilibrium does not arise, and in fact no solid is, as a rule, deposited until the solution has been cooled some 10° C. below the saturation temperature. When this degree of super-cooling has been reached a shower of minute crystals suddenly fills the liquid. These facts may be represented graphically by regarding a solid as having a double solubility curve as in Fig. 34. Under the conditions of temperature and concentration represented by the area A, crystallisation will take place only if the solid is present ; while the area B represents the conditions under which it will take place spontaneously. These areas are not sharply defined and have no theoretical justification. The phenomenon is of importance, however, in the practical preparation of good crystals.

It seems probable that the dust floating in air contains large numbers of *nuclei* of crystals of almost every kind. These nuclei are apparently minute crystals of, perhaps, a few dozen molecules. Their wide distribution is probably a consequence of their minute size, a very little of the substance being able to form an enormous number of nuclei. When substances are made for the first time, the air can contain no trace of their nuclei and they sometimes remain obstinately uncrystallisable. When they have been made half a dozen times in the laboratory the air contains nuclei of their crystals and no difficulty is found in crystallising the substances.

**101. Formation of Regular Crystals.**—In order that a few well-formed crystals should be obtained it is necessary to ensure that crystal nuclei are not present in too great numbers. In crystallising a salt it is best therefore not to use a solution which is so concentrated that the process of cooling to room temperature will cause *spontaneous* crystallisation (area B in diagram). A solution should be made up so as to be saturated about 10° C. above room temperature. It is then covered from dust and left overnight in a place where the temperature is even and which is free from draughts and vibration. Under these conditions only a few nuclei will enter from the air and on these will be produced small well-formed crystals, which should be removed before the temperature begins to rise as the next morning advances.

If it is desired to make larger crystals these small well-formed crystals are suspended by a hair in an open vessel containing a saturated solution of the substance to be crystallised. This solution must be kept at an even temperature preferably in a cellar or a thermostat. Gradual evaporation causes the solid to deposit slowly on the crystal without formation of fresh nuclei to act as crystal centres. A good method is to place the salt solution and crystal and also a dish of sulphuric acid under a bell-jar in a place free from vibration and even

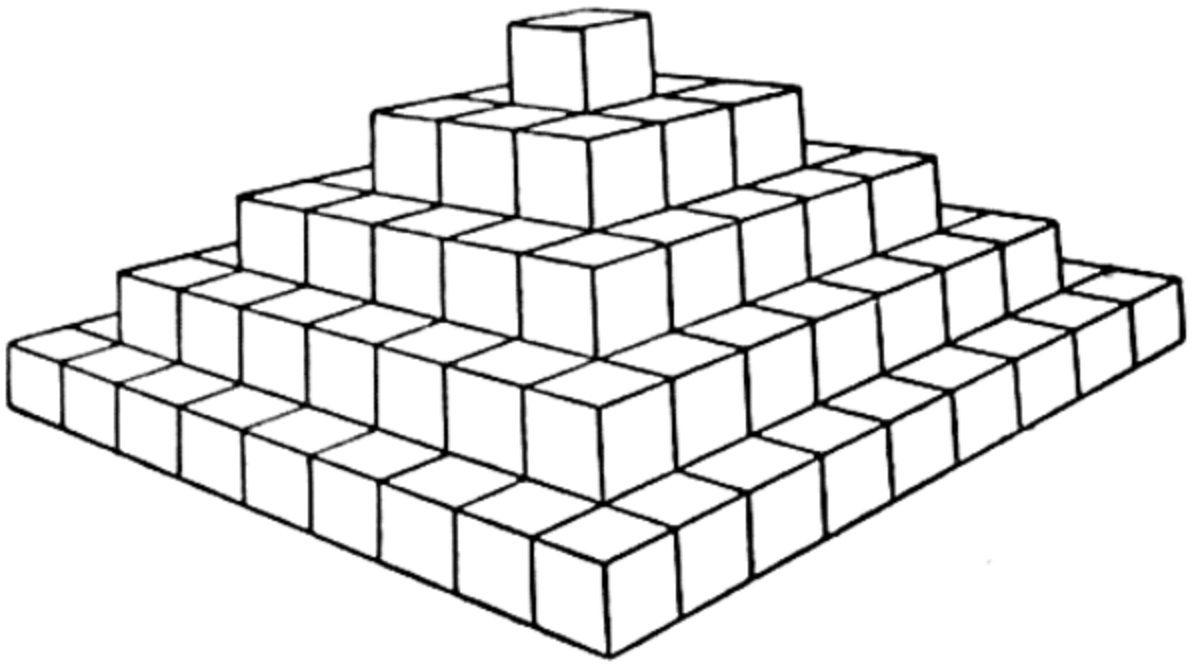


FIG. 35.—Pile of cubes reproducing crystal form.

in temperature. The sulphuric acid absorbs the water vapour and promotes rapid evaporation.

## STRUCTURE OF CRYSTALS.

**102. Space-lattice.**—It had been realised, since the earliest times of crystal-study, that crystal structure could be accounted for after a fashion by supposing that crystals were aggregates of particles arranged in an orderly manner in space. Haüy, "the father of crystallography," showed that simple geometrical solids such as cubes or spheres could be piled into patterns which

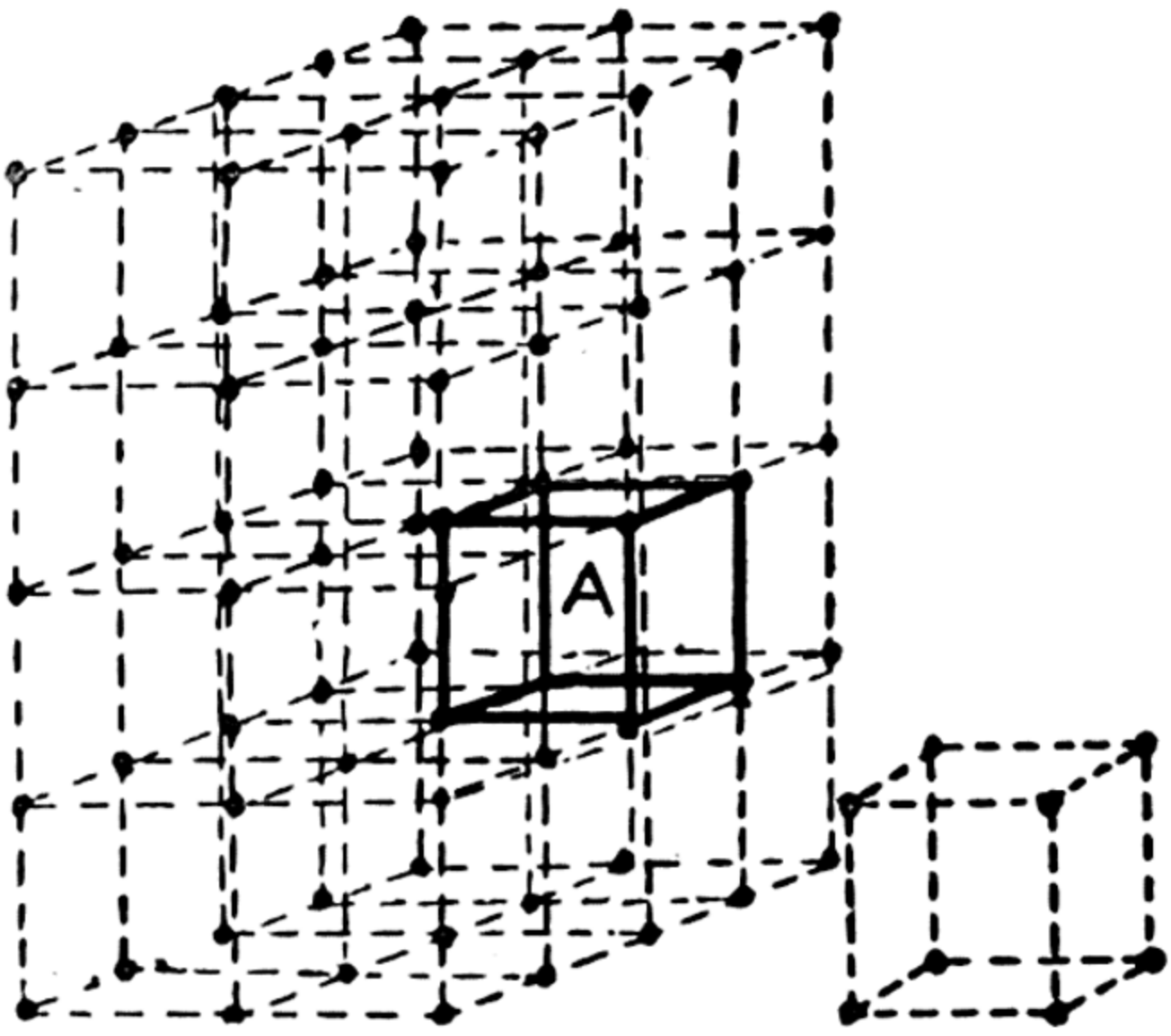



FIG. 36. Simple space-lattice of cubic type showing unit cell A.

reproduced various crystal forms, and thereby showed that an orderly arrangement of particles could produce bodies of regular form analogous to crystals.

We now believe that a crystal is made up of atoms, molecules or ions regularly arranged in contact. Two atoms, of course, cannot be in contact in the same sense as are the cubes of Fig. 35. The boundary of an atom or molecule is not a sharply defined surface : but if we accept an atom's boundaries as being at the half-way distance between the centres of two atoms brought as close to each other as electrical repulsion allows, it is true to say that the atoms in a crystal are in contact. The kinetic heat-movement of the atoms

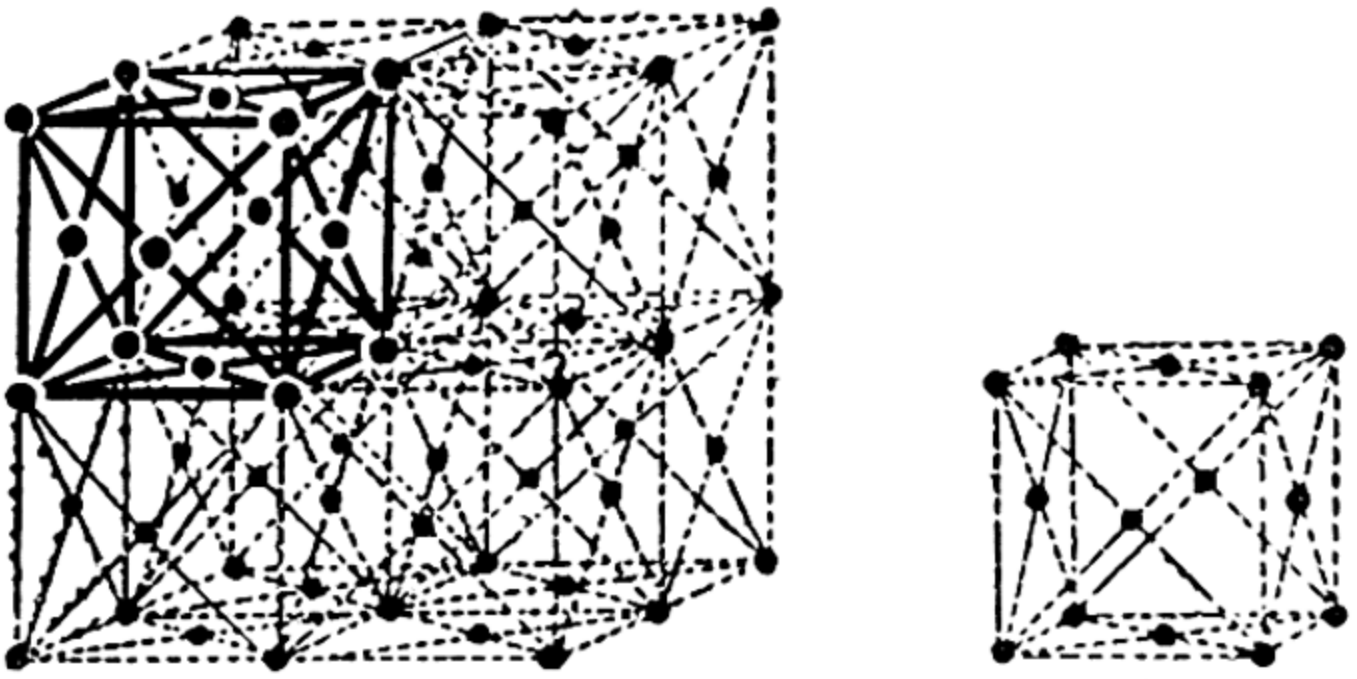


FIG. 37.—Another type of space-lattice, the face-centred cube.

does not require appreciable spaces between the atoms, for it is of very small amplitude.

Bravais assumed that a set of particles—actually atoms or molecules —was present in the crystal and that these were arranged in *space-lattices*. By a space-lattice is meant an arrangement of rows of points in three dimensions, such that the points form a series of ' cells ' consisting of parallelepipeda. The space-lattice is homogeneous, *i.e.*, the arrangement of points about any one point is the same as the arrangement about any other. Figs. 36, 37 illustrate more clearly than a short description what is meant by a space-lattice.

It can be shown that there can exist exactly two hundred and thirty fundamentally different types of space-lattice, and it was soon shown that if the molecules (or parts of molecules) in a crystal were arranged in these

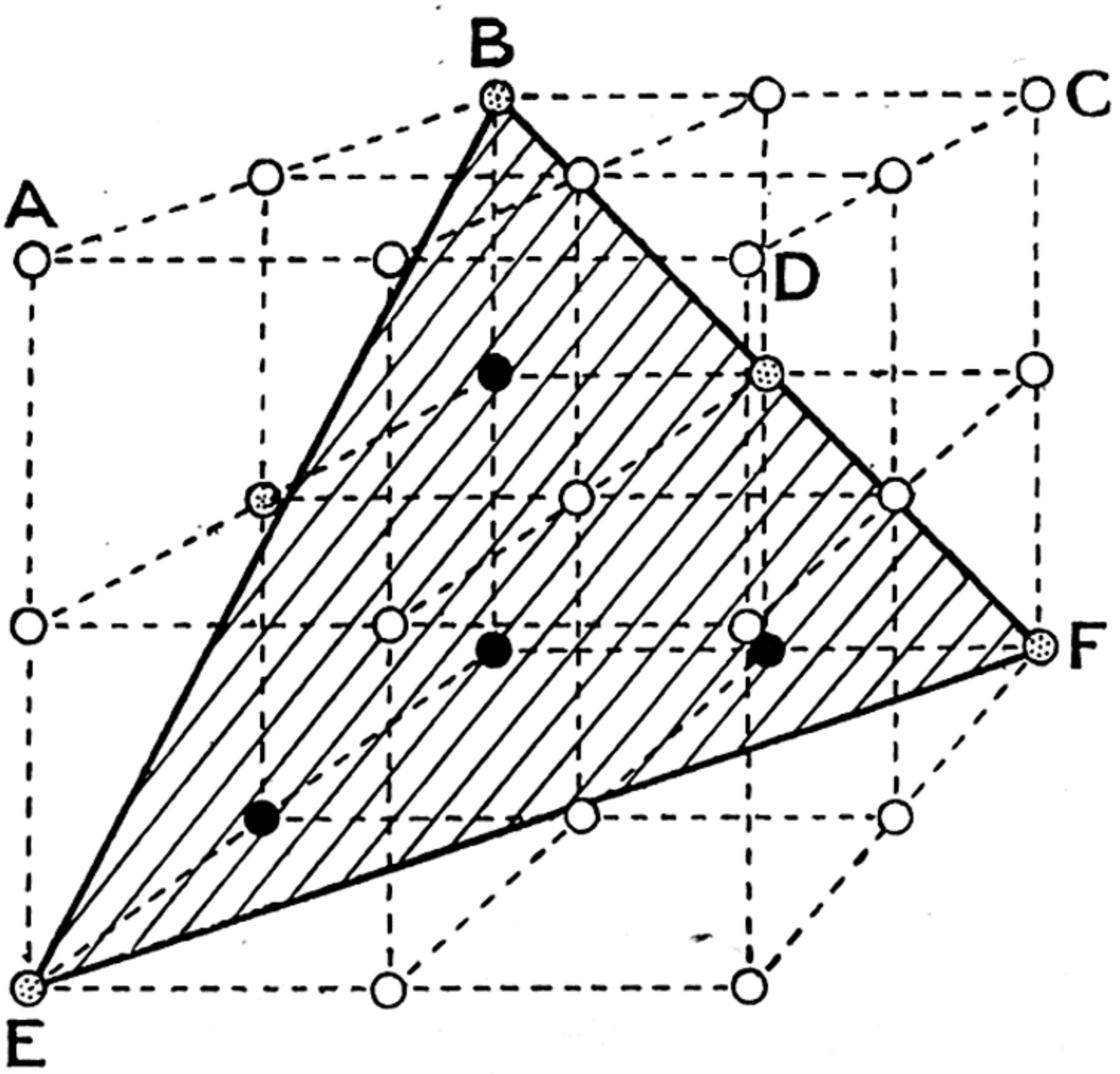



FIG. 38.—Possible crystal faces in a cubic space-lattice.
ABCD—cubic face.
BEF—octahedron face.

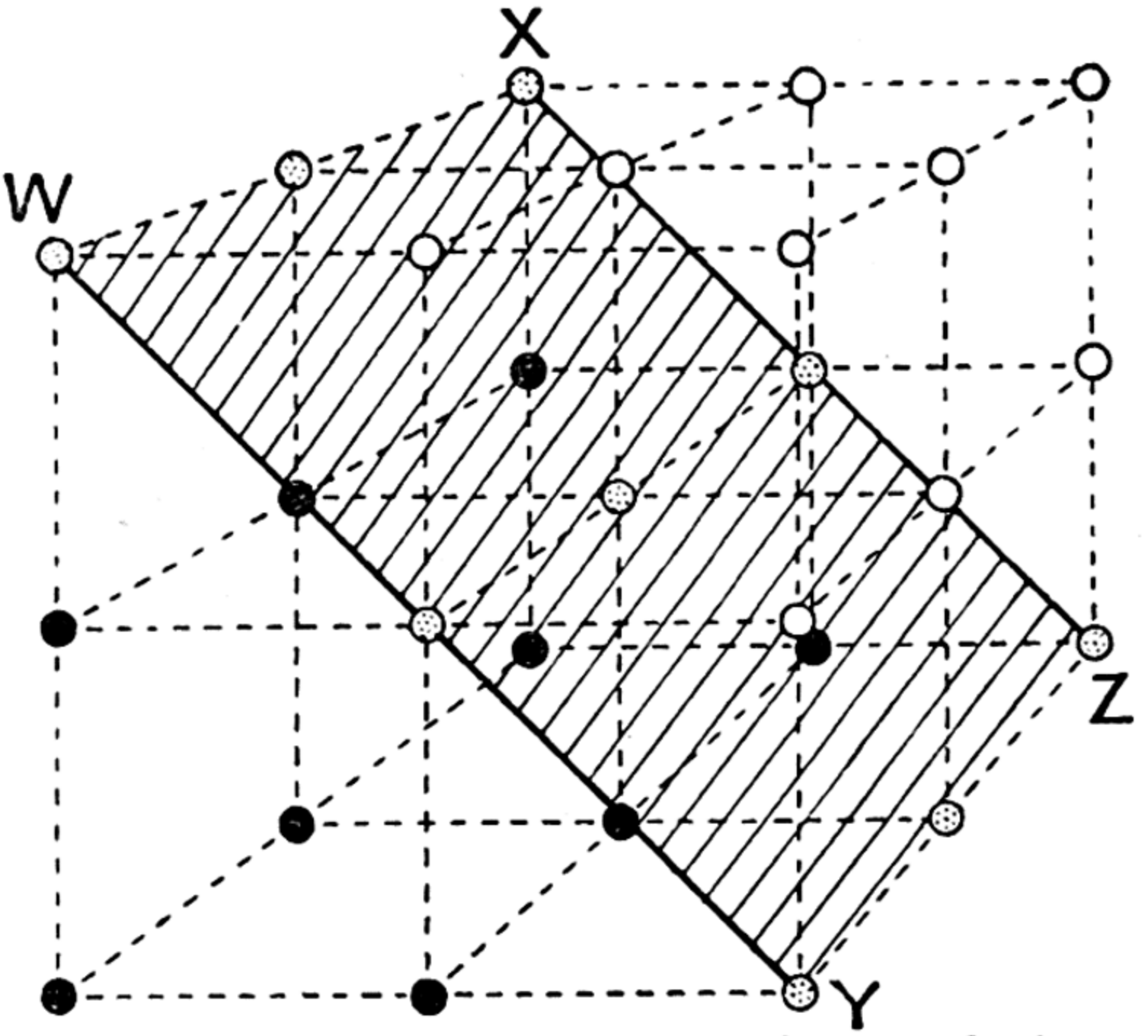



FIG. 38a.—Possible crystal faces in a cubic space-lattice.
WXYZ—another possible crystal face.

lattice systems the existence of the whole of the thirty-two classes of known crystals could be explained.

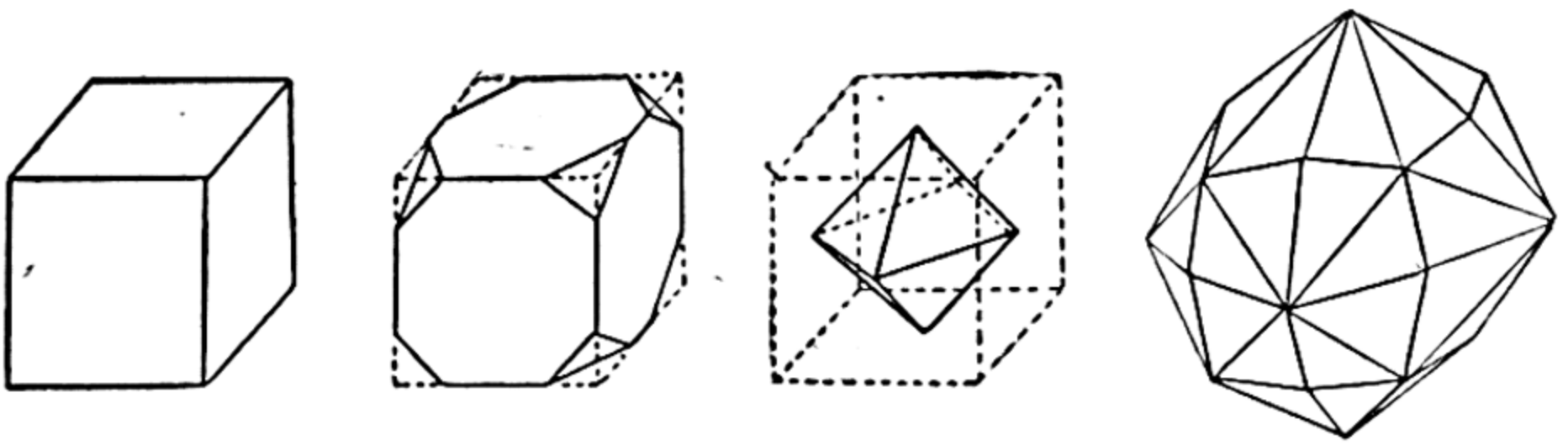
It was supposed that the faces of a crystal represented planes intersecting the lattice in such a way as to pass through a large number of lattice units (*i.e.*, or ions). Consider for example the simple cubic lattice shown in Fig. 38. Such a plane as ABCD represents the most probable crystal face, for it passes through the densest array of molecules possible. This lattice would be one of those possible for the cubic system, and faces based on planes, such as ABCD, would produce a cuboid. But such faces as these are not the only possibility. It is well known that many substances which crystallise in cubes can crystallise also in octahedra. Thus common salt crystallises in cubes from pure water, but as octahedra from water containing a trace of gelatine.

If we select as a possible crystal face the plane BEF, which contains the next greatest number of points (1 per 2 units of area) it will be seen that a crystal bounded by these faces will form an octahedron.

Thus the same lattice can account for two types of crystal, cubes and regular octahedra. This lattice can actually account for many more than these two simple types. Thus the diamond, which has a type of cubic space-lattice, often forms the remarkable hexakis-octahedra of forty-eight faces shown in Fig. 39.

In similar, though more complex fashion, it was established that all the patterns of crystal faces found in practice could be explained by the assumption that the crystals of any one system were based on a set of particular types of lattice all having the symmetry of that system.

This theory was worked out before any *direct* evidence as to internal structure of a crystal could be obtained. The remarkable work of Laue, Bragg and



Cube. | Cube showing octahedral faces. | Octahedron derived from cube. | Hexakis-octahedron.

FIG. 39.—Cubic crystals.

others on the reflection and diffraction of X-rays by crystals has now enabled us to ascertain directly the nature of these lattices which are the foundation of crystal structure.

**103. X-rays and Crystal Structure.**—In the year 1912 Dr. Laue, of Munich, discovered that the internal planes of molecules in the space-lattice structure of a crystal were capable of diffracting X-rays though they were not able to diffract light. X-rays are radiation of the same character as light but differ from it in having a wavelength not much greater than the diameter of an average molecule, while the wavelength of sodium light is about $6 \times 10^{-4}$ cm., about 5,000 times longer.

Laue's method of examining a crystal was to project into it a pencil of X-rays and receive the trace on a photographic plate. The pencil is broken up and a series of symmetrically arranged spots are obtained. The cause of this phenomenon was diffraction by the internal planes of molecules in the crystal, and each spot revealed by a mathematical analysis the position of an internal plane of molecules or possible crystal face. Plate X*a* shows a Laue photograph of the hexagonal mineral nepheline; the hexagonal symmetry of the spots is obvious.

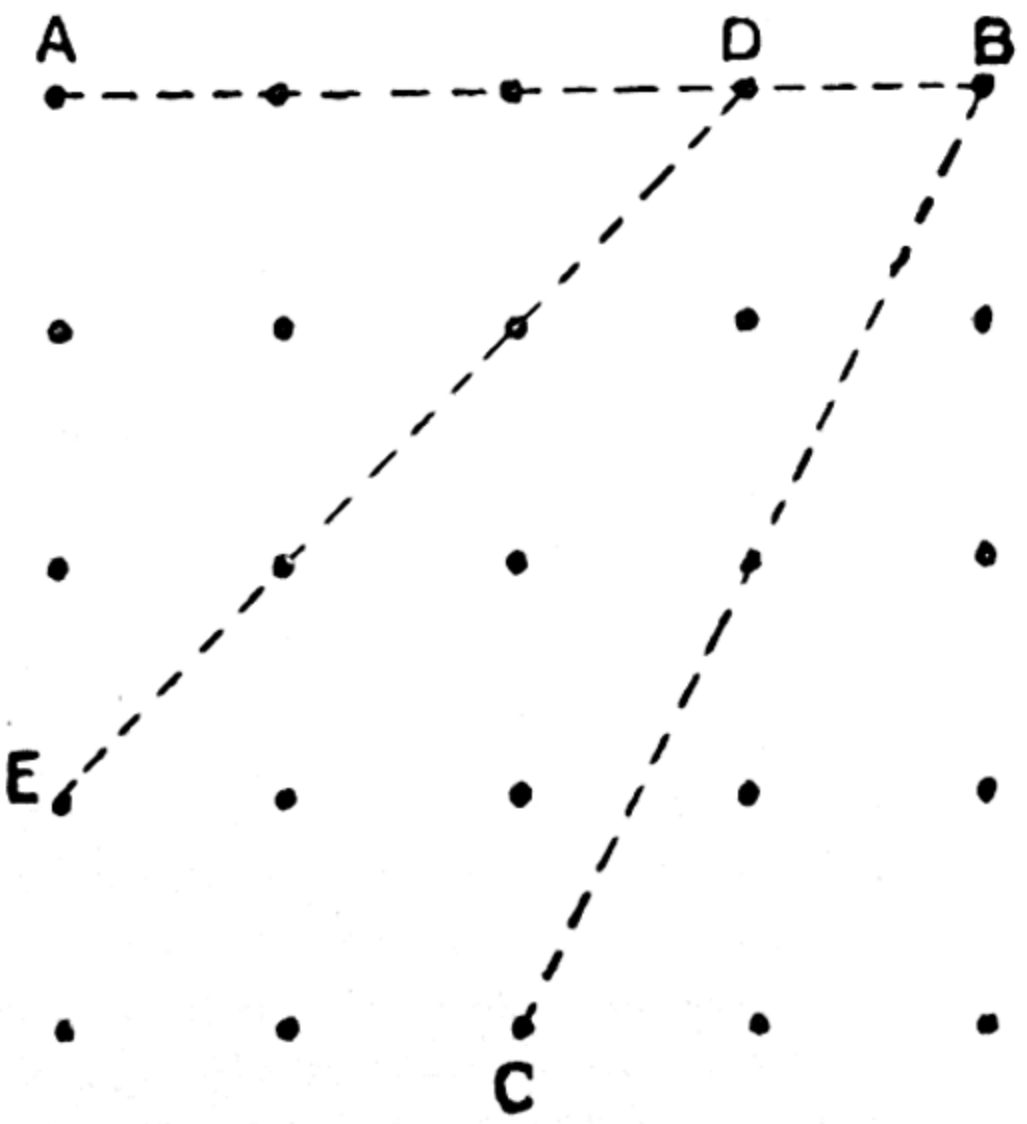



FIG. 40.—Section, cubic crystal. AB, DE, BC; planes at which reflection of X-ray can take place.

Sir William Bragg soon devised a second method of attacking the problem. Instead of using the crystal as a diffraction-grating, he obtained *reflections* of X-rays from its internal molecular planes. He projected a fine pencil of X-rays on to the crystals and measured the several angles at which it was reflected, these angles corresponding to the position of the internal planes (Fig. 40). In this way he obtained the position of the planes and also their distance apart. The latter value was obtained by the study of interference effects. From these data it is possible to map out the relative positions of and actual distances between the molecules or ions which constitute crystals.

It must suffice here to mention some of the remarkable results obtained. In the first place the work of Laue and Bragg entirely confirms the mathematical deduction that crystals consist of molecules or atoms arranged in space-lattices. More than this, it has thrown a good deal of light on the modes of combination of many chemical substances.

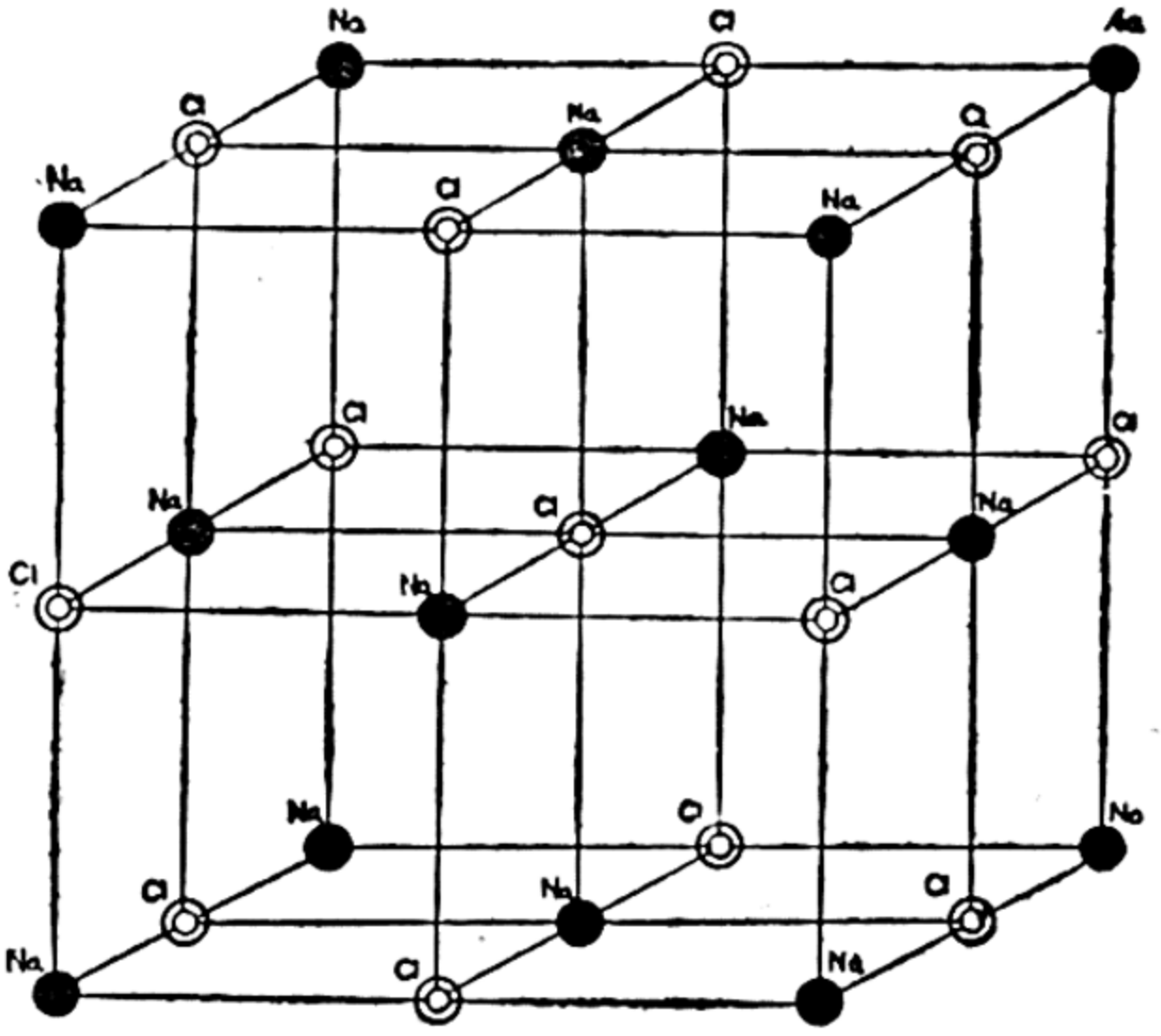



FIG. 41.—Structure of sodium chloride crystal.

*Crystals built up from ions.*

The study of the rock-salt crystal soon revealed that the units of which the lattice was built up were not NaCl molecules, for a study of the interference effects produced by reflection at successive planes showed that the octahedral planes of this substance were alternately of different materials, which appeared (from considerations of their reflecting power) to be sodium and chlorine atoms, or rather, ions.

It became clear that the structure of a sodium chloride crystal was that of Figs. 41, 42. The "cubic" planes contain both kinds of atoms and the octahedral planes only one kind. Moreover, every sodium atom is surrounded by six evenly-spaced chlorine atoms, and every chlorine atom by six evenly-spaced sodium atoms. The remarkable conclusion is then forced on us, that in such a crystal as that of sodium chloride the identity of each molecule is lost and no particular chlorine atom belongs to any particular sodium atom.

The study of other crystals of salts revealed a similar state of affairs. In each case the ions, but not necessarily all the atoms, were separate units. Thus,

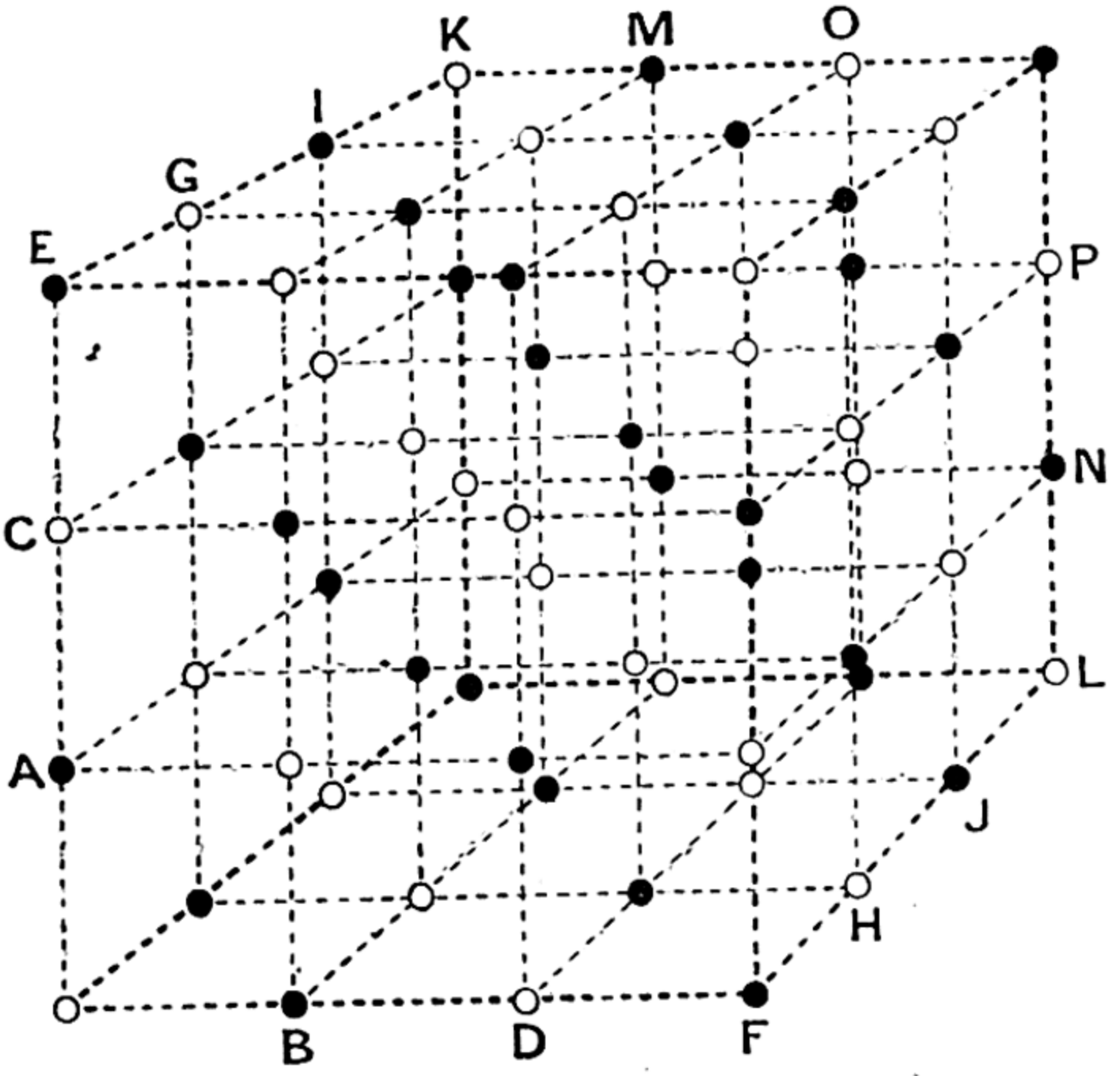



FIG. 42.—Structure of sodium chloride crystal.
Planes AB, EF, IJ, MN, contain only sodium atoms. CD, GH, KL, OP, contain only chlorine atoms. Sodium atom = ●, chlorine = ○

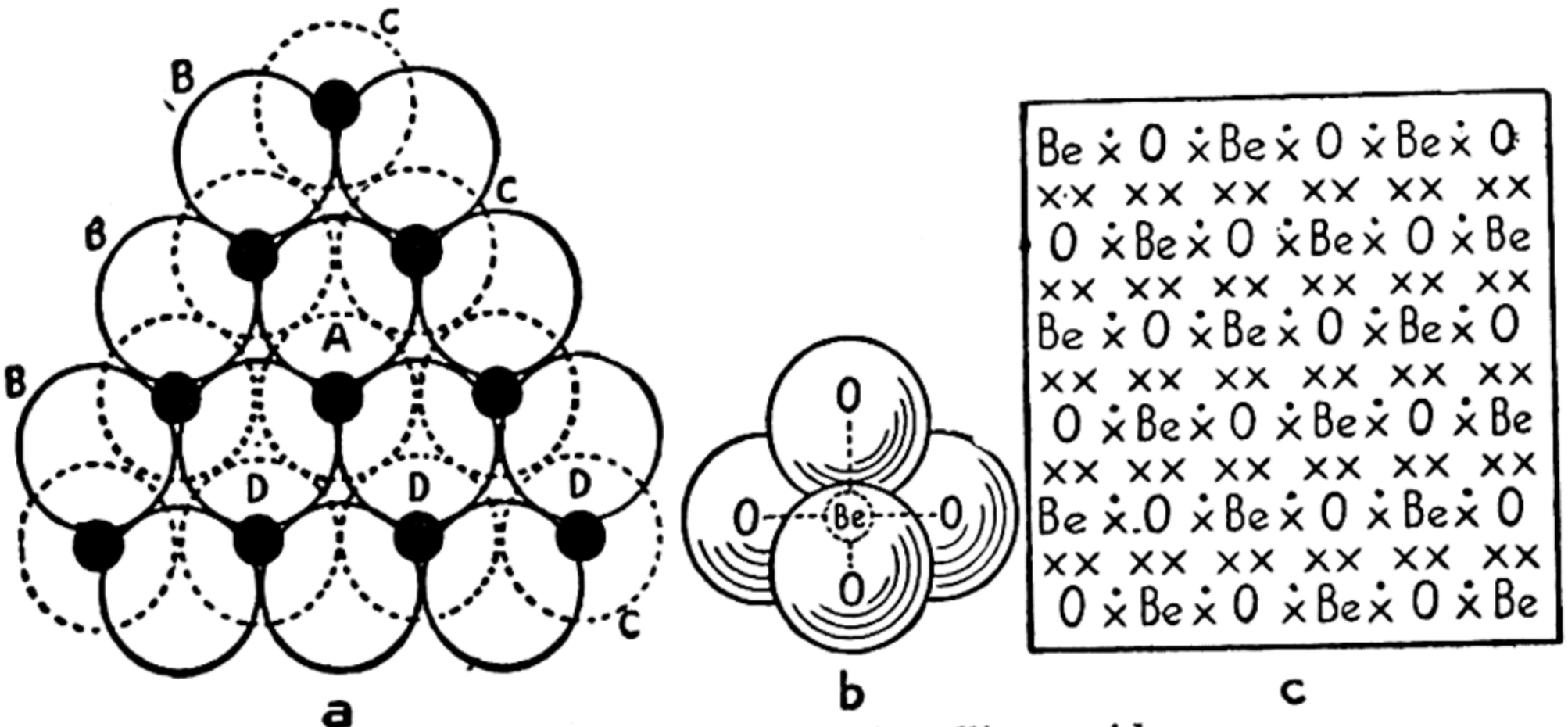



FIG. 43.—Structure of beryllium oxide.

(*a*) Plan. Black circles represent beryllium atoms; white circles represent oxygen atoms. (*b*) Beryllium atom co-ordinated to four oxygen atoms. (*c*) Showing the electronic linkages.

in calcite $CaCO_3$ the Ca ions and $CO_3$ groups form separate units, but the oxygen and carbon atoms are linked in such a way that each $CO_3$ group retains its individuality while in the crystal.

*Crystals built up from Molecules.*

The crystals of salts in general show lattices made up of individual ions. The crystals of non-ionisable compounds are of two types. In the first and most

usual, the unit is the molecule. Since the molecule in general has little attraction for a similar molecule, crystals of this type are usually soft and readily fusible or volatile. The crystals of such substances as sulphur, benzene, sulphur trioxide, chlorine, may provide examples.

These are in great contrast to the crystals of salts in which the ions are powerfully held together by the attraction of their opposite charges. The ions in salt-crystals are therefore hard to separate and true salts are usually of very high melting point and boiling point and fairly hard.

*Giant Molecules.*

The second type of crystal formed by non-ionisable compounds is the *giant molecule*. In such a crystal every atom is chemically combined by a covalent linkage with the next. The example of the diamond (§ 529a), of which the structure is shown on p. 409, illustrates the properties of great hardness and very high melting point and boiling point, which result from this very firm attachment of the atoms.

Other examples of giant molecules are afforded by the silicates (§ 599a) and by many metallic oxides, such as beryllia, alumina after ignition, etc. The hardness and infusibility connected with giant molecules is well illustrated by the latter.

These oxides form giant molecules by co-ordinate linkages from the oxygen atom to the metal atom. Thus beryllium oxide may have the structure illustrated in Fig. 43. The large white circles represent a layer of oxygen atoms (B, B) occupying the least amount of space possible. In half of the interstices between them are the small beryllium atoms, represented as black circles (D, D) : above these again is another layer of oxygen atoms, shown as broken white circles (C, C). Each beryllium atom is covalently linked to four oxygen atoms and each oxygen atom to four beryllium atoms. Alumina has a similar structure.

Since X-rays are reflected by the individual atoms and not the whole molecule, and since atoms differ much in their power of reflecting X-rays, it is possible to interpret the X-ray reflection spectrum of a complicated compound in such a way as to ascertain the positions of some or all of the atoms and distances. This has thrown much light on the structure of many complicated compounds, notably the polysilicates. the structure of which remained unsolved until the Braggs elucidated it in the work described in § 599a.

**103a. The Shape of Molecules.**—It will be seen that the above methods may give a general idea of the shape of a molecule and a very fair idea of the "lay-out" of such large molecules as those of the silicates, alum, etc., has been gained.

Small molecules cannot easily be treated in this way. However, the study of the spectra of the light diffracted by liquids (Raman spectra) and the study of infra-red spectral lines, which are brought about by the vibration and rotation of the whole molecule, have led to a few simple conclusions. In the first place, the shape of a molecule is not easily changed. The linkages will bend somewhat, but can only be stretched to a very small extent. Triatomic molecules are very rarely linear, carbon dioxide,

$$O = C = O,$$

and probably nitrous oxide, $N \equiv N \rightarrow O$, are the only common examples.

The majority have the end atoms at an angle of 100°–140°. The ammonia molecule forms a flat pyramid. Among the molecules whose forms have been studied are the following :—

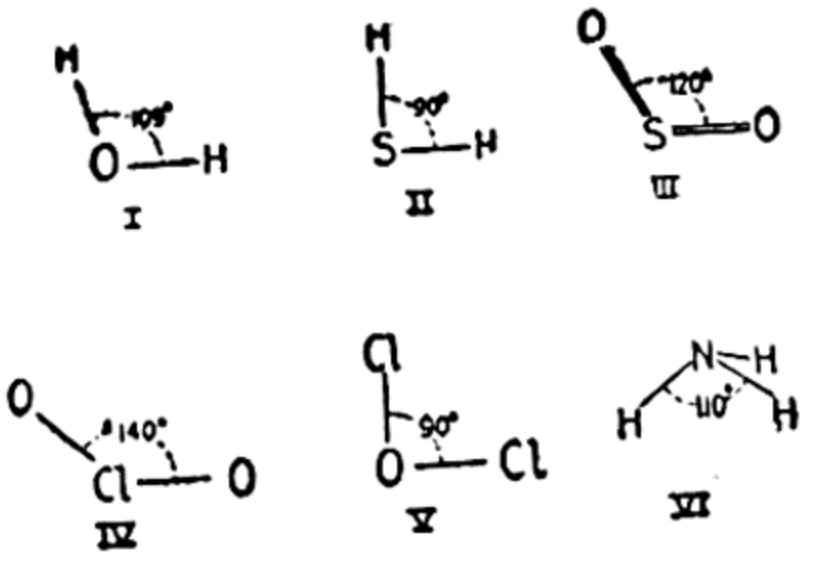



FIG. 44.—Shapes of simple molecules. Numbers I, II, and VI are drawn to a scale of roughly $10^8 : 1$.

# CHAPTER V

## THE RATE OF CHEMICAL REACTIONS AND CHEMICAL EQUILIBRIA

**104. Meaning of Rate of Reaction.**—The study of such a phenomenon as chemical change is not really begun until an attempt has been made to measure its extent or intensity. The three chief quantities which have been measured in connection with chemical reactions are: (1) The masses taking part in the change (pp. 32–43). (2) The energy evolved or absorbed (pp 29–32). (3) The rate at which the change takes place.

It is with the last of these that we now concern ourselves. By the rate of a reaction we mean *the quantity of material transformed in unit time.* The quantity of the reagents transformed is expressed in gram-molecules and the unit of time is usually the second. It will be seen at once that we cannot say that a *reaction*, say the decomposition of hydrogen peroxide,

$$2H_2O_2 = 2H_2O + O_2,$$

has any particular fixed velocity. The velocity of reaction of any particular lot of the material depends on a number of factors, such as the quantity of material present, its concentration, the temperature, etc.

**105. The Mechanism of Chemical Change.**—There is still a great deal of uncertainty as to the exact *mechanism* of chemical change, but some useful guidance can be gained from the kinetic theory and the many measurements of the rate of chemical reactions which have been made.

We picture a solid as an assembly of atoms and molecules ceaselessly vibrating but not altering their relative positions or arrangement. A liquid we regard as a concourse of atoms or molecules in chaotic motion, ceaselessly striking each other and rebounding, but held together by molecular attraction.

A gas we conceive as mainly consisting of empty space through which molecules are continuously flying, rebounding one against the other.

Now if chemical reaction between *two or more* substances is to take place it is evidently necessary that there should be either contact between the reacting molecules or at least an approach to an exceedingly short distance. If this is the case it is to be expected that chemical reaction between two solids should be very difficult to bring about, for two particles of solid can touch only at a few points and so their respective molecules cannot come into contact. On the other hand, liquids and gases should be able to react easily both

with solids and with each other. This is indeed the case, and the old adage, "*Corpora non agunt nisi fluida*" (Bodies do not react except in the fluid state, *e.g.*, as a gas or liquid), while not fully true, is very nearly so. Non-volatile solids react only if vigorously rubbed together or subjected to very great pressures.

If, then, it is a condition for chemical reaction that the two kinds of molecules concerned shall come into contact, we may deduce that anything which increases the number of collisions between the different kinds of molecules will also increase the rate of reaction. Now the number of collisions taking place can be influenced in two ways :

(1) The average distance of the molecules from each other may be made greater or less. This can be done in the case of a gas by decreasing or increasing the pressure upon it.

Suppose a particular molecule confined in a given space passed through a fixed point once per minute on an average. If the space through which it can travel is halved it will pass through the point twice as often. Now if two molecules are going to meet in a chemical reaction they must be at the same spot at the same time. If the volume of the gas is halved the chance of *each* molecule being at any particular spot at any particular time is doubled and, therefore, the chance of both molecules being at the same spot at the same time is multiplied by *four*.

Accordingly, where two kinds of molecules are present in a gas, the number of collisions between two molecules of different kinds varies as the square of the pressure, and where $n$ kinds of molecules are present the number of collisions between $n$ molecules of different kinds varies as the $n$th power of the pressure. Now, other things being equal, the more collisions there are between the molecules the more chemical reactions take place between them. It follows then that in a gas mixture where $n$ molecules are required to meet to produce a chemical reaction, the rate of the reaction (*i.e.*, the quantity of material transformed in a given time) will be proportional to the $n$th power of the pressure.

(2) The number of collisions taking place between different kinds of molecules is influenced by the numbers of each kind present.

A little thought will show that the chance of a molecule of one kind hitting a molecule of another kind depends on the numbers of both of them present in a given space. For, using the same argument as before, if we require two molecules of different kinds to meet, the chance of a molecule of the first kind being at a particular spot is proportional to the number of that kind of molecule within reach of it, and in the same way the probability of a molecule of the second kind being there also depends on the number of that kind of molecule within reach of it.

**106. The Law of Mass Action.**—These facts were expressed by Guldberg and Waage in the Law of Mass Action, which lays down that—

**The rate of a chemical reaction is proportional to the concentrations of each of the reacting components.**

This does not mean that the rate of reaction is proportional to the *weights* of the reacting substances present, but to the *numbers of each kind of molecule present in a given volume.* Now one gram-molecule of any substance contains the same number of molecules (c. $6{\cdot}06 \times 10^{23}$) and we can therefore express our *concentrations* as gram-molecules per litre.

The Law of Mass Action does not tell us anything about the absolute rate of reaction, which must be determined by experiment. It tells us only how the rate will alter according to the concentration and proportions of the reacting substances.

Experiment entirely confirms the Law of Mass Action, and the success of the theory of equilibria developed from it (§ 110) is an additional argument in its favour.

**107. Effect of Temperature on the Speed of a Chemical Reaction.**—The effect of a rise of temperature on a chemical reaction is invariably to increase the rate of reaction. According to the kinetic theory a rise of temperature increases the velocity of the molecules and, therefore, the number of collisions taking place between them. This increase can be calculated, and accounts for an increase of the rate of a chemical reaction amounting to some 2 per cent. per degree centigrade. Now the rate of increase of the velocity of a chemical reaction is actually from 10 to 20 per cent. per degree centigrade.

The cause of this apparent discrepancy is the fact that not all collisions of molecules capable of reacting result in a chemical reaction. Thus in a mixture of hydrogen and chlorine in diffused daylight (§ 1047) each hydrogen molecule hits a chlorine molecule about a billion times every second, but most of the hydrogen and chlorine molecules are still unchanged after an hour ! Thus in a case like this combination takes place only where a collision occurs in such a way that the molecules are able to react. We do not know much about the conditions which lead to two molecules combining when they collide, but it is thought that the quantity of their *internal energy* resulting from the relative movements of the atoms and electrons which compose the molecules is the chief influence. From a study of specific heats it is clear that by no means all the heat which enters a body goes to increase the external motion of the molecules. A certain proportion is used up in increasing the internal energy of the molecules, and it is probably this internal energy which influences the rate of reaction so greatly.

**108. Catalysis.**—The speed of chemical reactions is not only influenced by temperature and pressure ; for in many cases the presence of some substance which apparently takes no part in the

reaction has a remarkable effect on the reaction velocity. This phenomenon is known as catalysis[1] and the substance accelerating (or retarding) the chemical reaction is called a catalyst.

*A catalyst may be defined as a substance which, when present in comparatively small proportion, influences the speed of a chemical reaction without itself being altered in quantity or chemical composition.*

The influence may be positive or negative, may accelerate or retard the reaction. There is controversy on the point as to whether the catalyst can start a reaction or only accelerate a reaction which is already in progress. Certain chemical reactions appear to be started by a catalyst, but these are often said to be reactions already in progress at an immeasurably slow speed. The distinction between a reaction so slow that we cannot detect its rate of reaction, and a reaction which is not taking place is clearly only theoretical.

A catalyst may accelerate or retard a reaction, but is considered to be unable to influence the final state of equilibrium, *i.e.*, to catalyse one of two opposing reactions to a greater extent than the other. Ostwald proved this theoretically, but it is still disputed whether his assumptions are valid for all cases.

Cases of catalysis fall into two groups, *homogeneous* and *heterogeneous* catalysis. The first are cases in which the catalyst is not separated by any bounding surface from the reaction mixture. A typical example is the catalysis of the reaction of ethyl acetate and water to alcohol and acetic acid by, say, hydrochloric acid.

$$C_2H_5.O.CO.CH_3 + H_2O \rightleftharpoons C_2H_5OH + CH_3.COOH.$$

The addition of hydrochloric acid may cause the rate of the decomposition to increase more than a hundred times.

Again, carbon monoxide and oxygen will not react when heated unless a trace of water vapour is present.

In *heterogeneous catalysis* the catalyst is marked off from the reaction mixture by a surface. Examples are the catalysis of the reaction between sulphur dioxide and oxygen by platinum, or the decomposition of hydrogen peroxide in presence of the same metal.

The action of catalysts is believed to depend :

(1) On the formation of unstable 'intermediate' or 'carrier' compounds.

(2) On the condensation of a layer of the reacting products at a high concentration at or near the surface of the catalyst.

**109. Types of Catalyst.**—Most reactions may be catalysed and many types of substance may act as catalysts (*i.e.*, alter the velocity of some reaction), but none the less there are certain types of substance which act as catalysts in a marked degree. These are :

(1) Compounds which are readily oxidised and again restored by

[1] Gk, *κατάλυσις*, an "unloosing."

reduction or *vice versa*. These include compounds of elements of easily variable valency, chief among which are the 'transition' elements of the periodic table and certain other substances, such as bromine and iodine.

A typical example of catalysis brought about by such compounds is the catalytic effect of cobalt hydroxide in bringing about the decomposition of hypochlorites. If we add a few drops of cobalt sulphate to a warm solution of sodium hypochlorite oxygen is rapidly evolved. The final result of the reaction is expressed by

$$2NaOCl = 2NaCl + O_2,$$

but the actual process is probably

(*a*) The formation of cobalt hydroxide with the alkali present

$$CoSO_4 + 2NaOH = Na_2SO_4 + Co(OH)_2$$

(*b*) The reaction of the hypochlorite and cobaltous hydroxide to form cobaltic hydroxide

$$NaOCl + H_2O + 2Co(OH)_2 = NaCl + 2Co(OH)_3.$$

(*c*) The decomposition of the unstable cobaltic hydroxide into cobaltous hydroxide and oxygen.

$$2\,Co(OH)_3 = 2Co(OH)_2 + O + H_2O.$$

The cobaltous hydroxide is then re-oxidised by more of the hypochlorite and the whole process is repeated.

As a second example we may take the catalysis of the reaction of nitric acid and sulphur by bromine. If nitric acid is heated with sulphur the reaction is very slow, but if a little bromine is added the reaction is much accelerated. None of the bromine is used up in the reaction.

The process is probably :

(*a*) Formation of a sulphur bromide

$$2S + Br_2 = S_2Br_2.$$

(*b*) The decomposition of this by water to sulphur, sulphur dioxide and hydrobromic acid

$$2S_2Br_2 + 2H_2O = SO_2 + 4HBr + 3S.$$

(*c*) The oxidation of the sulphur dioxide to sulphuric acid

$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2.$$

(*d*) The oxidation of the hydrobromic acid and restoration of the original bromine

$$2HNO_3 + 2HBr = 2H_2O + 2NO_2 + Br_2.$$

The bromine then combines with more sulphur and the above reactions again take place.

(2) *Hydrogen ion* is one of the most effective of catalysts. A great number of reactions are accelerated or retarded by the presence of acid, the mechanism usually consisting in the formation of an intermediate ion.

The reaction of water with the organic substances known as esters and analogous to inorganic salts is strongly catalysed in this way. Thus the reaction of ethyl acetate and water to form ethyl hydroxide (alcohol) and acetic acid

$$C_2H_5O.OC.CH_3 + H.OH \rightleftharpoons C_2H_5OH + HO.OC.CH_3,$$

proceeds hundreds of times more rapidly if hydrion (derived from an acid) be present.

(3) *Water* has been termed a universal catalyst. It has been stated that the majority of reactions are slowed up almost to cessation by the complete removal of water from the reacting substances; but the reliability of much of this work is not beyond question. The whole question of "intensive drying" is discussed in the chapter on Water, §§ 204–207.

(4) *Metals*, notably the transition elements of the eighth group of the periodic table.

Some of the substances mentioned above as catalysts probably act by forming 'intermediate' or 'carrier' compounds with the reacting substances. A large group of catalysts, including most of those of the highest industrial importance, appear to act in a quite different manner. Certain metals, notably platinum, palladium, nickel, cobalt, iron and copper, are exceedingly effective catalysts for reactions in which gases, more particularly hydrogen, are concerned. Among important reactions catalysed in this way may be mentioned:

(*a*) $2H_2 + O_2 = 2H_2O$, catalysed by platinum . *v.* § 1228
(*b*) $2SO_2 + O_2 \rightleftharpoons 2SO_3$, catalysed by platinum . *v.* § 930
(*c*) $C_2H_4 + H_2 = C_2H_6$, catalysed by nickel . *v.* § 1202
(*d*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$, catalysed by iron. . *v.* § 689

It seems on the face of it very improbable that an element such as platinum, which forms compounds only with the most reactive substances, should form a large series of compounds with the very various reaction mixtures which are catalysed when passed over it. It is, of course, possible to *say* that in reaction (*b*) platinum oxide is formed and decomposed.

(1) $Pt + O_2 = PtO_2.$
(2) $PtO_2 + 2SO_2 = Pt + 2SO_3,$

but since there is no evidence that platinum forms an oxide under these conditions this theory is rightly rejected.

The most probable explanation of the activity of these metals is connected with the fact that they have the power of adsorbing considerable volumes of gases. It is thought that the gases of the reaction mixture are condensed on the surface or dissolved in the surface layer of the metal. In this way the concentration of the reaction mixture is greatly increased and the reaction is thereby accelerated.

This is certainly not the whole story, for the increase of velocity is too great to be accounted for in this way. Moreover, the fact that different metallic catalysts may cause different products to be produced from the same reagents is very difficult to explain.

Thus a mixture of carbon monoxide and hydrogen passed over a heated catalyst gives :

(1) With a copper catalyst at 300° C. mainly formaldehyde,

$$CO + H_2 = CH_2O.$$

(2) With a catalyst of zinc and chromium oxides at 300°–358° C., chiefly methyl alcohol,

$$CO + 2H_2 = CH_4O.$$

(3) With a catalyst of finely-divided nickel at 150°–200° C., chiefly methane,

$$CO + 3H_2 = CH_4 + H_2O.$$

The chief theories of catalysis are discussed in works on Physical Chemistry. A good general idea of the various causes of catalysis can be put forward, but it is rarely possible to predict theoretically the quantitative effect of a catalyst on a reaction.

The road to a better understanding of catalysis is a clearer knowledge of what happens when two molecules react—a knowledge which we are slowly gaining.

No single explanation of catalysis can ever be given, for the term groups together a large and varied collection of mechanisms which probably have little in common save their result, the acceleration or retardation of a reaction.

## Chemical Equilibrium

**110. Reversible Reactions.**—It is not uncommon to find that the products of a reaction themselves react, forming the original reagents once more. Thus, if hydrogen and iodine vapour are heated to 400° C. they combine, forming hydrogen iodide.

(1) $$H_2 + I_2 \rightarrow 2HI,$$

while hydrogen iodide itself decomposes at this temperature, forming hydrogen and iodine.

$$2HI \rightarrow H_2 + I_2. \quad (2)$$

Thus at 400° C. *both* reactions will proceed simultaneously and hydrogen, iodine, and hydrogen iodide will always be present. We symbolise these processes as

$$H_2 + I_2 \rightleftharpoons 2HI.$$

From the Law of Mass Action it follows that the speeds of these reactions will depend on the quantities of the reagents present.

Now the substances which react most quickly will disappear most quickly. These will therefore be diminished in quantity and, as time goes on, will react more slowly. So the quantities of the reacting substances will alter, until a state is reached when the forward reaction (1) is proceeding at the same speed as the reverse reaction (2), and all the substances taking part in the reaction are disappearing at the same rate as that at which they are being formed. The substances are then said to be at *equilibrium*.

We may now express these facts in general terms. If one or more substances undergo a chemical reaction, forming products which themselves react, in such a way as once more to form the original substances, the reaction is said to be *reversible*. If the substances are called A and B and the products C and D, there are clearly two reactions in progress *at the same time* :

$$\text{(i)}\ A + B \rightarrow C + D.$$
$$\text{(ii)}\ C + D \rightarrow A + B.$$

These two reactions are symbolised by the equation,

$$A + B \rightleftharpoons C + D.$$

Since both products and original substances are reacting to form each other, the final result will be a mixture containing *all* the products and original substances in proportions depending on the concentrations of the reagents, the temperature, and, above all, the nature of the substances used.

The paramount guide in the study of reversible reactions is the Law of Mass Action. Symbolically expressed, the Law of Mass Action states that in any chemical reaction

$$A + B + C + \ldots, \text{etc.} = E + F + G + \ldots, \text{etc.}$$

the velocity ($v$) of the reaction is directly proportional to the *active masses* of the reacting substances, *i.e.*, to their concentrations expressed in *gram-molecules* per litre.

$$v = k[A]\,[B]\,[C]^1 \text{ etc.} \quad \ldots\ldots\ (a)$$

If two or more molecules of the same substance take part they are to be regarded as separate molecular species. Thus the reaction

$$2A + 3B = C + D + E \text{ etc.}$$

may be written $A + A + B + B + B = C + D + E$ etc.

$[A]$ is to be read as " the concentration of A."

and so $V = k[A][A][B][B][B]$
$= k[A]^2[B]^3$

This equation may be applied to an equilibrium reaction.

Let the substances P, Q, R, etc., be in chemical equilibrium with the substances S, T, U, etc.,

$$P + Q + R \ldots \text{etc.} \rightleftharpoons S + T + U \ldots \text{etc.}$$

Then two reactions are going on simultaneously :

$$P + Q + R + \ldots \text{etc.} \rightarrow S + T + U + \ldots \text{etc.} \quad . \quad . \quad . \quad (b)$$

and
$$S + T + U + \ldots \text{etc.} \rightarrow P + Q + R + \ldots \text{etc.} \quad . \quad . \quad . \quad (c)$$

Then by the Law of Mass Action, which leads to equation (*a*) above, the velocities $v_1$, $v_2$ of the reactions (*b*) and (*c*) are given by

$$v_1 = k'[P][Q][R] \ldots \text{etc.} \quad . \quad . \quad . \quad . \quad . \quad (d)$$

and
$$v_2 = k''[S][T][U] \ldots \text{etc.} \quad . \quad . \quad . \quad . \quad . \quad (e)$$

When equilibrium is reached there is no further change in the concentrations of the substances. It therefore follows that the rate of transformation of P, Q, R into S, T, U is, at equilibrium, the *same* as the rate of transformation of S, T, U into P, Q, R. and therefore that $v_1 = v_2$.

If $v_1 = v_2$ at equilibrium, then also

$$k'[P][Q][R] \ldots \text{etc.} = k''[S][T][U] \ldots \text{etc.}$$

and
$$\frac{[P][Q][R][\text{etc.}]}{[S][T][U][\text{etc.}]} = \frac{k''}{k'} = K,$$

The constant K is called the *equilibrium constant* : it has a fixed value for any specified reaction under specified conditions of temperature.

We can now enunciate the very important *Equilibrium Law of Mass Action*, which can be deduced by the above arguments and also, quite independently, by thermodynamical methods.

*In any mixture at chemical equilibrium the ratio of the product of the concentrations of the reactants to the product of the concentrations of the substances produced is equal to a constant, known as the equilibrium constant, the value of which depends on the temperature and the nature of the reaction.*

The general equation
$$\frac{[P][Q][R][\text{etc.}]}{[S][T][U][\text{etc.}]} = K,$$

which applies to all mixtures which have reached chemical equilibrium, is of great importance as enabling us to predict the effect of alterations of the concentration of one or more substances upon the concentrations of the other compounds present in an equilibrium mixture.

Let us consider the way in which this equation may be applied to a simple equilibrium reaction.

We will take as illustration the simple type of bi-molecular reaction represented by the equation

$$A + B \rightleftharpoons C + D.$$

(1) *To predict the effect of the addition of a reacting component (say A) to the equilibrium mixture, the total volume remaining unchanged.*

From a consideration of the Law of Mass Action we may write the equation connecting the concentrations of the reacting substances at equilibrium,

$$\frac{[A][B]}{[C][D]} = K.$$

If we add A, we increase the concentration of A, *i.e.*, [A]. The equation can then only be satisfied by an increase of [C] or [D] or a decrease of [B] or all of these. This can only come about by the substance B reacting with A and forming C and D.

Thus the addition of a reacting substance to an equilibrium mixture brings about a decrease in the concentrations of the substances with which it reacts, and an increase in the concentrations of the products of this reaction.

(2) *Removal of a reacting substance* (*say* C) *from an equilibrium mixture* (*without altering the volume*).

As before:

$$\frac{[A]\,[B]}{[C]\,[D]} = K.$$

If C is removed, then [C] becomes smaller, and [D] must increase and [A] and [B] decrease. This is effected by the further reaction of A and B to form C and D.

Thus the removal of a reacting substance from an equilibrium mixture brings about a decrease of concentration of the substances which react to form it, and an increase of concentration of the substances with which it reacts.

(3) *Effect of altering the pressure in a gas mixture at chemical equilibrium.*

The effect of altering the pressure depends on whether any change of volume results from the chemical reaction.

In such a reaction as

$$\underset{1\text{ vol.}}{H_2} + \underset{1\text{ vol.}}{I_2} \rightleftharpoons \underset{2\text{ vols.}}{2HI}$$

there is no volume change. From the equation above,

$$\frac{[H_2]\,[I_2]}{[HI]^2} = K.$$

Suppose the pressure to be increased $n$ times. Then each of the concentrations is increased $n$ times and the fraction becomes

$$\frac{n\,[H_2].n\,[I_2]}{n^2[HI]^2},$$

which is still equal to K, and the concentrations are still such as to satisfy the equilibrium equation. Pressure therefore does not affect the equilibrium in this case.

Suppose, however, there is a change in volume in the reaction, as in the case of the reaction of nitrogen and hydrogen to form ammonia

$$N_2 + 3H_2 \rightleftharpoons 2NH_3.$$

$$\frac{[N_2]\,[H_2]^3}{[NH_3]^2} = K.$$

Let the pressure be increased $n$ times. Then each of the concentrations is increased $n$ times and the fraction becomes

$$\frac{n[N_2]\,n^3[H_2]^3}{n^2[NH_3]^2}$$

which is $n^2$ times its original value, which was equal to K. To restore equilibrium nitrogen and hydrogen must combine, forming ammonia, and equilibrium will be reached when $[NH_3]$ has been sufficiently increased and $[N_2]$ and

$[H_2]$ sufficiently diminished to make the value of the above fraction once more equal to K. The law of van't Hoff and Le Chatelier (§ 111) may also be used to predict the effect of pressure on equilibrium. An *increase* of pressure will cause the equilibrium to shift in such a way that the volume is *diminished* and the increase of pressure minimised, and a decrease of pressure will act in the opposite direction.

It will easily be seen that the effect of altering the concentration of a solution is exactly analogous to an alteration in pressure. Thus, diluting a solution will cause a dissolved substance to dissociate.

**111. Effect of Temperature on Chemical Equilibrium.**—We have seen that equilibrium is attained when the velocities of two opposing reactions become equal. Reactions are always accelerated by an increase of temperature, but no two reactions are influenced to the same extent. A change of temperature will, therefore, always increase the velocities of the two opposing reactions of an equilibrium to unequal extents, and the concentrations of the substances present at equilibrium will alter until the velocities of these reactions again become equal. The final result of the change can be predicted if the heat of reaction is known.

The Law of van't Hoff and Le Chatelier states that: *If any constraint is placed upon a system at equilibrium, the equilibrium will shift in such a sense as to oppose the effect of the constraint.*

Thus, if an equilibrium mixture is *heated*, the equilibrium will shift in such a way that *heat is absorbed*. If the mixture is *cooled*, the equilibrium will shift in such a way that *heat is given out* and the extent of the cooling consequently diminished.

A case in point is the equilibrium between nitrogen, oxygen and nitric oxide:

$$N_2 + O_2 \rightleftharpoons 2NO - 43200 \text{ cals.}$$

A rise in temperature will cause the equilibrium to shift in the direction which will cause heat to be absorbed, and this effect will be brought about by nitrogen and oxygen combining to form nitric oxide. A rise of temperature, therefore, favours the formation of nitric oxide.

# CHAPTER VI

## IONIC THEORY OF SOLUTION

**112. The Decomposition of Substances by the Electric Current.**—If a source of electricity, such as an accumulator, be connected to two thin plates of platinum immersed in a dilute solution of copper sulphate a chemical change in the latter at once takes place. On the plate connected to the positive pole of the battery bubbles of gas appear which, when collected, prove to be oxygen. On the plate connected to the negative pole there appears a pink film of the metal

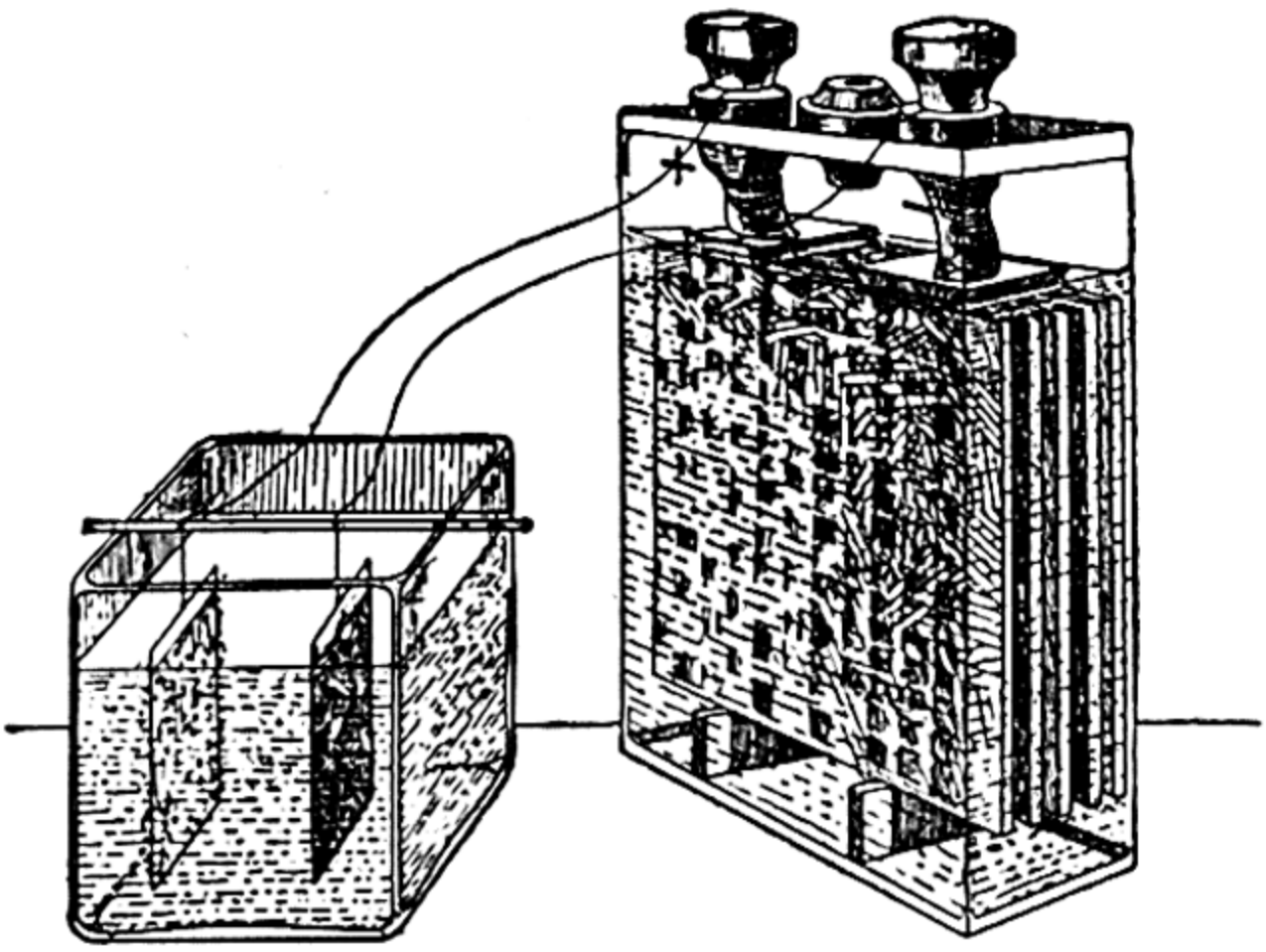


FIG. 45.—Electrolysis of copper sulphate.

copper. If the current is maintained for a sufficient time the blue colour of the copper sulphate solution disappears and a solution of sulphuric acid remains. If we surround the positive plate with a porous cell we can prove that it is only at this plate that the sulphuric acid is produced. The whole chemical change might be represented by the equation

$$2CuSO_4 + 2H_2O = 2Cu + 2H_2SO_4 + O_2,$$

but it is obvious that this equation leaves unexplained several remarkable facts about the process. The chief peculiarities which mark off such a change as we have described from ordinary chemical reactions are :—

(1) The necessity for the use of electricity.

(2) The fact that the products appear in widely separated parts of the reaction-vessel.

The decomposition of a substance by the action of the electric current is called *electrolysis* ; the substance decomposed is called an *electrolyte* ; the conductors, maintained at a potential difference, at which the products of the decomposition appear, are called the *electrodes*. The electrode connected to the negative source of current is the *cathode* and that connected to the positive source is the *anode*.

**113. Faraday's Laws of Electrolysis.**—It was known in the eighteenth century that electricity could decompose chemical substances, and Davy at the beginning of the nineteenth century, after the invention of the voltaic pile, made a considerable quali-tative study of its action and thereby isolated many new substances. The first systematic and quantitative study was that of Faraday. Faraday accounted for the motion of the products of electrolysis to the plates connected to the positive and negative poles of the battery by supposing that the electrolyte (acid, alkali or salt)

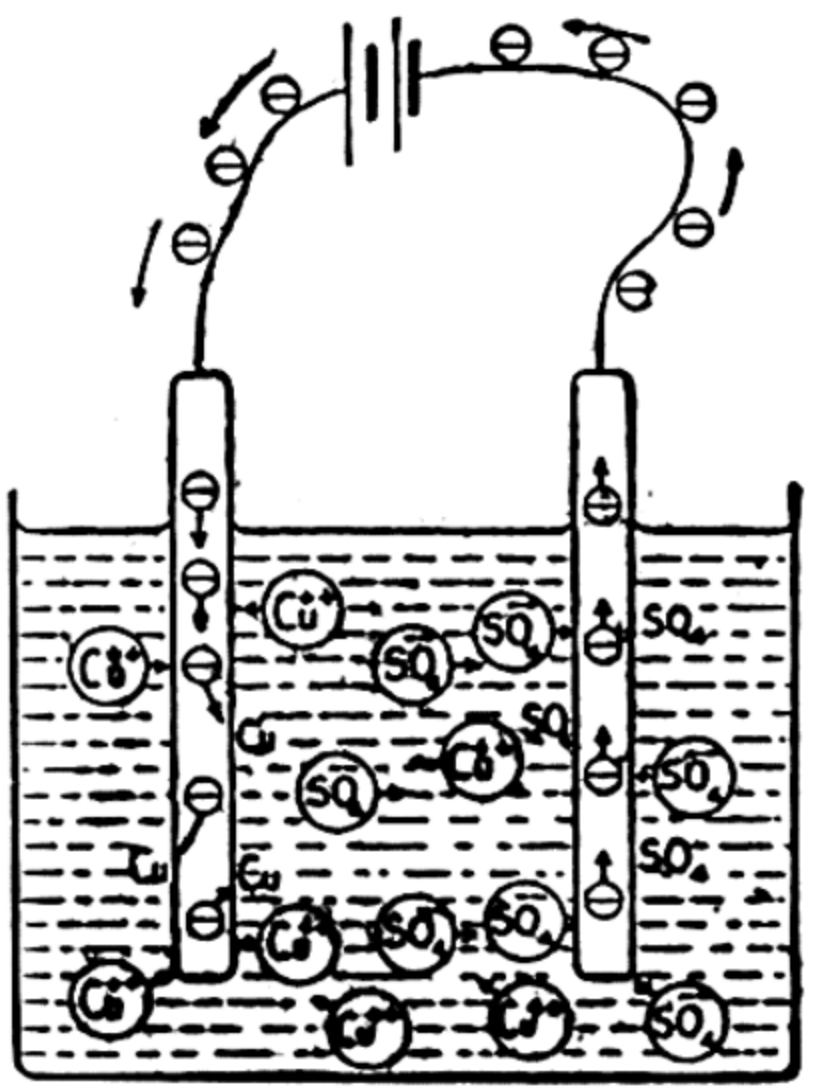



FIG. 46.—Diagram showing electrolysis of copper sulphate solution. The charged ions wander to the poles of opposite sign and there give up or receive electrons, themselves becoming electrically neutral. (⊖ represents an electron *i.e.* a single negative charge).

was separated by the action of the electric current into electrically-charged radicals, which he termed *ions*. Thus Faraday supposed that on electrolysis a salt, such as sodium chloride (NaCl), broke up into electrically-charged particles or ions ($Na^+$ and $Cl^-$). These he supposed to travel, as a result of their respective charges, to the oppositely-charged anode and cathode and by their motion

to conduct the current. When the ions reached the electrode they were discharged and appeared as sodium and chlorine respectively. This theory of electrolysis is very little different from that held to-day, the only divergence being that we do not regard the ions as being *produced* by the current, but as existing preformed in the solution.

Faraday studied the phenomena of electrolysis from the quantitative point of view and discovered two laws of fundamental importance. These are :—

**(1) The mass of the substance decomposed is directly proportional to the quantity of electricity passing through the solution.**

**(2) The masses of substances deposited by the same current are in the proportion of their chemical equivalent weights.**

Both laws may be expressed in the statement that **one gram-equivalent of any substance is liberated by the passage of 96,494 coulombs of electricity.**

These laws are readily explained if we suppose that every ion has a total charge equal to a small constant value, $e$ (the electronic charge) multiplied by its valency. Since the current passes only by the discharge of the ions the quantity of electricity passing is proportional to the number of ions discharged and therefore, also, to the mass of substance produced (Law I.).

A quantity of electricity equal to a single ionic charge $e$ will liberate the quantity of material which has this same electric charge. If all ions had the same charge $e$, one molecule would always be liberated by a current of value $e$. But an ion's charge is $e \times$ *valency* and so the quantity liberated by a current of value $e$ is the weight of the ion divided by the valency, *i.e.*, one equivalent. This is, in fact, what is stated in Faraday's second Law of Electrolysis.

**114. The Ionic Theory of Solution.**—Faraday's theory of electrolysis has certain defects. In the first place, if it were the electromotive force which separates the molecules of the electrolyte into ions, no electrolysis should take place unless the E.M.F. is enough to overcome the attraction which holds the parts of the molecule together. Actually, if polarisation is excluded, *any E.M.F., however small*, will bring about electrolysis, a fact which suggests that the ions are not formed by the current, but merely attracted to the poles. On these grounds Clausius, in 1857, concluded that a solution of an electrolyte must always contain a certain proportion of *free ions*. Clausius thought of this proportion as a small one, but Arrhenius, in 1887, realised that there was a connection between the abnormally low molecular weights of electrolytes in solution (§ 116 (3) ) and the existence of free ions.

The Ionic Theory, as put forward by Arrhenius, stated that all

electrolytes in solution are partly dissociated into ions. These ions consist of atoms or groups of atoms (the acid or basic radicals of the electrolyte) with a charge due to the presence in or absence from the atom or group of as many electrical charges as the ion has valencies. The total charge of the ions formed from any substance is algebraically equal to zero. A few examples are illustrated below.

Ostwald supposed that the decomposition of a molecule into ions was a partial and reversible reaction which (like all dissociations) is most complete at great dilutions. This is believed to be true for

| Electrolyte. | Electropositive ions. | Electronegative ions. |
|---|---|---|
| HCl | $H^+$ | $Cl^-$ |
| NaOH | $Na^+$ | $OH^-$ |
| NaCl | $Na^+$ | $Cl^-$ |
| $H_2SO_4$ | $H^+$, $H^+$ | $HSO_4^-$, $SO_4^{--}$ |
| $Ba(OH)_2$ | $Ba^{++}$ | $OH^-$, $OH^-$ |
| $CaCl_2$ | $Ca^{++}$ | $Cl^-$, $Cl^-$ |
| $Na_2HPO_4$ | $Na^+$, $Na^+$, $H^+$ | $HPO_4^{--}$, $PO_4^{---}$ |

weak acids and bases which are but slightly dissociated ; thus only about 1 per cent. of acetic acid or ammonia in a tenth normal solution is in the form of ions. Strong acids, strong bases and nearly all salts are believed to be wholly dissociated into ions under all conditions.

If we write the equation for the dissociation of a weak electrolyte AB into ions $A^+$ and $B^-$ in the form

$$AB \rightleftharpoons A^+ + B^-$$

according to the Law of Mass Action

$$\frac{[A^+]\,[B^-]}{[AB]} = k.$$

The equilibrium constant $k$ is in this case called the *dissociation constant* of the electrolyte.

The dissociation constant of electrolytes varies very widely. Very strong electrolytes do not give a satisfactory constant, and it is clear that their dissociation does not follow the scheme indicated above. Weak electrolytes, however, obey it very well, and the list of dissociation constants given below gives an idea of the proportion of these substances dissociated.

*Dissociation Constants of Weak Electrolytes.*

| Electrolyte. | Dissociation Constant (25° C.) |
|---|---|
| Sulphurous acid | $1{\cdot}7 \times 10^{-2}$ |
| Acetic acid | $1{\cdot}86 \times 10^{-5}$ |
| Carbonic acid | $3 \times 10^{-7}$ |
| Boric acid | $6{\cdot}5 \times 10^{-11}$ |
| Ammonium hydroxide | $1{\cdot}8 \times 10^{-5}$ |

The fact that the ionisation of strong electrolytes does not appear to obey the Law of Mass Action while that of weak electrolytes obeys it well has given rise to much discussion and research over a period of many years. Several theories have been put forward to the effect that strong electrolytes are wholly dissociated in solution. Debye and Hückel have calculated the conductivities of dilute solutions of strong electrolytes on this basis. While the conductivity figures for concentrated solutions of strong electrolytes cannot be interpreted satisfactorily according to any theory, the figures for the heats of neutralisation of acids and alkalis (see § 117 (5) ) and also the additive properties of strong electrolytes seem to indicate complete dissociation at concentrations up to half-normal or normal.

The ionic theory explains a large number of facts, amongst which are prominent the remarkable properties manifested by solutions of polar compounds, acids, alkalis and salts.

**115. Peculiarities of Acids, Alkalis and Salts.**—It is very noticeable that the classes of chemical compounds known as acids, alkalis and salts have a number of peculiar properties. Acids, alkalis and salts differ from other chemical compounds in the important particulars set out below. We may take the example of copper sulphate as characteristic of the class of acids, alkalis and salts, and that of sugar as characteristic of the other chemical compounds.

(1) **Acids, Bases and Salts are Electrolytes.**—Solutions of acids, alkalis and salts conduct electricity and are at the same time decomposed. A solution of copper sulphate conducts electricity and is changed at the same time into metallic copper and sulphuric acid. A solution of sugar, on the other hand, does not conduct electricity better than pure water.

(2) **The Properties of Acids, Bases and Salts are Additive.**—Thus the properties of a solution of copper sulphate are made up of two sets of properties, the first characteristic of a solution of a copper salt, the second characteristic of a solution of a sulphate; and it has hardly any properties characteristic of itself alone.

Such a compound as methane $CH_4$, carbon hydride, has, on the contrary, characteristic properties of its own, and its properties are not by any means all comprised in those of carbon compounds and those of hydrides.

(3) **Low Apparent Molecular Weight of Acids, Alkalis and Salts.**—

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All acids and alkalis, except the weakest, and all salts[1] show an abnormally high osmotic pressure and an abnormally low molecular weight in solution in water. In nearly all other solvents the molecular weights are those to be expected from the chemical formula, gas-density, etc. Thus hydrochloric acid as a gas appears by such methods as those described in §§ 51, 55 to have a molecular weight of 36·5, but hydrochloric acid in solution has, according to the cryoscopic method (§ 60), a molecular weight of about 19. It is found that the apparent molecular weight of an acid, alkali or salt in solution shows different values in solutions of different strengths, the lowest being in very dilute solution. This lowest apparent molecular weight tends to a value $\frac{M}{n}$ where $M$ is the true molecular weight and $n$ is the number of radicals present in the acid, alkali or salt.

(4) **Rapidity of Reactions between Acids, Alkalis and Salts.**—Acids, alkalis and salts very readily undergo double decomposition (§ 26) and react with each other almost instantaneously. Thus the reaction of the salts, sodium chloride and silver nitrate,

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl\downarrow$$

completes itself in a small fraction of a second while the analogous reaction of silver nitrate and ethyl chloride, which is not a salt or an electrolyte,

$$C_2H_5Cl + AgNO_3 \rightarrow C_2H_5NO_3 + AgCl,$$

proceeds quite slowly even on warming.

(5) **Identical Heat of Reaction of all Strong Acids and Strong Bases in Dilute Solution.**—The heat of reaction between dilute solutions of any strong acid and strong alkali is the same (13,700 cals.). The heats of all other types of reactions vary with the substances which react.

**116. Electrolytes.** Substances are electrolysed only in the liquid state. Thus solid salts, gases, etc., do not undergo electrolysis. Moreover, only certain well defined classes of chemical compounds can be electrolysed at all. These are :—

(1) Solutions of acids, alkalis, and salts.
(2) Fused alkalis and salts.

It is characteristic of such compounds that their molecules consist of two distinct portions, an *acid radical* and a *basic radical* (Chapter VIII), and the process of electrolysis appears to separate these portions of the molecule and set them free at the electrodes. In aqueous solution the situation is more complicated, for water itself

[1] But see §§ 427, 443.

is both an acid and a base, ionising, to some extent into, $H^+$ ions and $OH^-$ ions.

$$H_2O \rightleftharpoons H^+ + OH^-$$

The degree of this dissociation is small, and so pure water has only a minute conductivity. But hydrogen and hydroxyl ions from the dissociation of the water are present when a solution of a salt is electrolysed, and thus there are two sorts of positive ions and two sorts of negative ions in the medium. Which of the two positive ions, and which of the two negative ions, are discharged on electrolysis depends on the electrode potentials of the ions concerned, or, what is the same thing, their position in the electrochemical series (§ 126).

Thus in a solution of copper sulphate there are $H^+$ ions, $Cu^{++}$ ions, $OH^-$ ions and $SO_4^{--}$ ions. With platinum electrodes copper is deposited on the cathode, as $Cu^{++}$ ions are more easily discharged than $H^+$ ions, and oxygen is evolved from the anode, as hydroxyl ions are more easily discharged than sulphate ions, and the hydroxyl radicals formed when they are discharged combine with one another to give oxygen and water.

$$OH^- = OH + e$$
$$4OH = O_2 + 2H_2O$$

Conversely in a solution of sodium chloride the hydrogen ions are more easily discharged than $Na^+$ ions, and chloride ions more easily than hydroxyl ions. Thus the electrolysis of sodium chloride solution gives hydrogen and chlorine, whereas the electrolysis of *fused* sodium chloride (§ 223), gives sodium and chlorine, as only sodium and chlorine ions are present in the fused salt.

When copper electrodes are used in the electrolysis of copper sulphate solution, copper dissolves off the anode and is deposited on the cathode. This is the basis of the electrolytic refinement of copper (§ 276). At the anode three reactions are possible :—

$$(1)\quad OH^- = OH + e$$
$$(2)\quad SO_4^{--} = SO_4 + 2e$$
$$(3)\quad Cu = Cu^{++} + 2e$$

The third proceeds at a lower potential than the other two, and so all the copper dissolves off the anode before either of the other two reactions commence. The same type of reaction is possible with platinum electrodes, but the potential so high that the first reaction proceeds instead.

**117. Short Summary of Evidence for the Ionic Theory.**[1]—(1) In the

[1] A text-book of physical chemistry should be consulted, for space forbids a detailed discussion of the evidence.

first place it provides an explanation of the phenomenon of electrolysis in some respects more satisfactory than the older theory of Faraday, and in addition clearly explains the behaviour of voltaic cells in producing electricity (§ 123).

(2) Secondly, the ionic theory explains the fact that the conductivity of a solution per gram-equivalent of electrolyte present increases as it is diluted. Thus 2 c.c. of N/20 acetic acid conduct better than 1 c.c. of N/10 acetic acid, under comparable conditions. Though both contain the same amount of the acid the weaker solution contains a greater number of ions, for the degree of ionisation increases with dilution.

(3) The fact that electrolytes in solution consist to a large extent of ions separate and uncombined, accounts for the additive properties of their solutions (§ 174). Since, for example, all copper salts in dilute solution consist of copper ion $Cu^{++}$ and an acid radical, they will all manifest the properties characteristic of copper ion, *e.g.*, blue colour, poisonous character, etc.

(4) The abnormally low molecular weight of electrolytes in solution is explained by their dissociation into ions. The pressure of a gas (§ 43) depends on the temperature and also on the number of particles present in a given space. It appears that the same is true for the osmotic pressure of a solution (§ 56). If the substance is dissociated, more particles are produced and the pressure is higher ; consequently the molecular weight calculated from it will appear abnormally low.

(5) The fact that the heat of neutralisation of any strong base by any strong acid amounts to 13,700 cals., irrespective of the base and acid used, is very readily explained by the ionic theory and is very hard to explain in any other way, thus affording a strong piece of evidence.

Thus the ionic theory leads us to suppose that any strong acid, HA, in solution consists entirely or almost entirely of ions, in this case $H^+$ and $A^-$. In the same way a dilute solution of a base, MOH, consists of $M^+$ and $OH^-$. When these react, a salt, MA, is formed which, by the ionic theory, will consist in dilute solution of $M^+$ and $A^-$ ions. The reaction which we ordinarily write as

$$HA + MOH = MA + H_2O$$

is then actually

$$H^+ + A^- + M^+ + OH^- = M^+ + A^- + H_2O$$

or, striking out the substances appearing on both sides of the equation,

$$H^+ + OH^- = H_2O.$$

Thus any reaction between a *strong* acid and a *strong* base in *dilute* solution is simply the reaction of hydrion and hydroxyl ion to water and has, therefore, the same heat of reaction 13,700 cals. If the acid or base is weak it must dissociate before it can react, and varying amounts of heat are produced or absorbed by this dissociation. Thus the heat of neutralisation of a weak acid or base is not always the same.

The evidence which has in the past been adduced against the ionic theory is now for the most part considered valueless, and the theory is generally accepted. The laws which govern the conductivities and apparent molecular weights of strong electrolytes are not fully understood as yet, but the general theory as set out above is an integral part of the fabric of modern chemistry.

**118. Common Ion Effect.**—A number of interesting phenomena are caused by the "common ion effect."

When a weak acid or base is partly ionised in solution in water,

$$AB \rightleftharpoons A^+ + B^-,$$

it follows from the law of mass action that

$$\frac{[A^+]\,[B^-]}{[AB]} = k.$$

The constant $k$ is the dissociation constant. The addition of either $A^+$ or $B^-$ in the form of an electrolyte yielding these ions will increase the concentration of $A^+$ or $B^-$, and therefore (§ 110) will cause $A^+$ to combine with $B^-$ and form more of the undissociated AB.

So in general when to a solution of an electrolyte there is added a sufficient quantity of a common ion to increase the concentration of the latter, the proportion of the electrolyte in the undissociated state will be increased and the proportion of the other ions diminished.

Thus, for example, on adding strong sodium acetate solution to acetic acid we greatly increase the concentration of acetanion, and thereby increase the proportion of acetic acid and diminish that of hydrion.

If the solution is nearly saturated with the electrolyte, the latter may be precipitated as a result of its increase in concentration. Consider a saturated solution in contact with the solid. If the electrolyte is a weak one, the solid is in equilibrium both with the dissolved undissociated substance and with the ions formed from it.

$$AB \rightleftharpoons AB \rightleftharpoons A^+ + B^-.$$
Solid. Saturated solution.

If the electrolyte is a strong one and is wholly dissociated the solid will be in direct equilibrium with the ions.

$$AB \rightleftharpoons A^+ + B^-.$$
Solid. Ions in solution.

If either $[A^+]$ or $[B^-]$ is increased, [AB] is increased also, which, since the solution is already saturated, must result in separation of solid AB. As long as the solution is saturated [AB] must remain constant, and since

$$[A^+]\,[B^-] = k\,[AB],$$
$$[A^+]\,[B^-] = S,$$

where $S$ is a constant. This constant is known as the *solubility product*, and it will be seen that *a condition for saturation of a solution is that the product of the concentration of the ions should reach the solubility product.*

Thus, for example, the solubility product of ferrous sulphide is $1{\cdot}5 \times 10^{-19}$, and as soon as the product of the concentrations of ferrous ion and sulphide ion reaches this value in any solution solid ferrous sulphide will separate therefrom.

The arguments by means of which we have proved these formulæ apply only to weak electrolytes which are partially dissociated. It can be shown, however, that the formulæ will hold with fair accuracy for strong electrolytes also.

**119. Precipitation.**—A substance is precipitated when its solution becomes supersaturated. The attainment of the solubility product by the product of the concentrations of the ions is, therefore, the condition for precipitation. This fact is of great importance in analysis, where differences of solubility product are the basis of all qualitative work.

Consider, for example, the sulphides of the metals. The solubility products of a few of these are given below. The condition that they should be precipitated is that the product of the concentrations of the metal ions and of the sulphide ion should reach the solubility product. In a saturated solution of hydrogen sulphide there is a molar concentration of sulphide ion[1] of about $10^{-8}$, and in a solution of $H_2S$ to which has been added enough hydrochloric acid to make it twice normal, the concentration of sulphide ion is about $10^{-20}$ (see p. 140).

From the table below it will at once be clear that all the sulphides in the table are at any rate partly precipitated by neutral hydrogen sulphide solution, while the sulphides of copper and cadmium, but not those of iron and manganese, are precipitated by the hydrogen sulphide and hydrochloric acid mixture.

| | Solubility product. | Conc. of $S^{--}$ ion needed to ppt. a 1/10 normal solution.[2] |
|---|---|---|
| Copper sulphide . . | $8{\cdot}5 \times 10^{-45}$ | $8{\cdot}5 \times 10^{-44}$ |
| Cadmium sulphide . . | $3{\cdot}6 \times 10^{-29}$ | $3{\cdot}6 \times 10^{-28}$ |
| Ferrous sulphide . . | $1{\cdot}5 \times 10^{-19}$ | $1{\cdot}5 \times 10^{-18}$ |
| Manganous sulphide . . | $1{\cdot}4 \times 10^{-15}$ | $1{\cdot}4 \times 10^{-14}$ |

Similar considerations give us the reason for the precipitation of the hydroxides of iron, aluminium and chromium (but not those of manganese, cobalt, nickel, zinc, calcium, etc.), by ammonia in presence of ammonium chloride.

**120. Solution of Precipitates.**—Just as the addition of a common ion will cause precipitation of an electrolyte, so the removal of a common ion will cause it to dissolve. Consider a solid in contact with its solution,

$$AB \rightleftharpoons A^+ + B^-.$$

Solid.

If, say, $A^+$ is removed, solid AB will dissolve and dissociate to restore the equilibrium.

Ions may be removed from a solution by the addition of a common ion to a substance furnishing the ion in question. As an example let us consider magnesium hydroxide in contact with 1/10 normal ammonia solution at 18° C. The dissociation constant of ammonium hydroxide is about $1{\cdot}8 \times 10^{-5}$ at this temperature. The solubility product of magnesium hydroxide is $1{\cdot}2 \times 10^{-11}$ at 18° C.

$\therefore [Mg^{++}][OH^-]^2 = 1{\cdot}2 \times 10^{-11}$ when the solution is saturated with magnesium hydroxide.

1/10 normal ammonia solution has at 18° C. a concentration of hydroxyl on of about $10^{-3}$, and so we may see that magnesium hydroxide will remain precipitated if

[1] These figures are only approximate. The degree of dissociation of hydrogen sulphide is not very accurately known and varies with the temperature.

[2] Assumed completely ionised.

$$[Mg^{++}] = \frac{1{\cdot}2 \times 10^{-11}}{10^{-6}}$$

$$= \text{about } 10^{-5} \text{ gm.-mols. per litre.}$$

A quite dilute solution of a magnesium salt will therefore be precipitated by 1/10 normal ammonia.

We now add to the solution an equal volume of twice-normal ammonium chloride solution. This increases the concentration of $NH_4^+$ from about $10^{-3}$ to about 1, *i.e.*, increases it about 1,000 times.

From the equation

$$\frac{[NH_4^+]\,[OH^-]}{[NH_4OH]} = 1{\cdot}8 \times 10^{-5},$$

it will follow that the $[OH^-]$ will be correspondingly reduced to about $10^{-5}$. The condition for precipitation will then be that

$$[Mg^{++}] = \frac{1{\cdot}2 \times 10^{-11}}{10^{-12}}$$

$$= \text{appr. } 12.$$

It will then follow that a solution of a magnesium salt of less concentration than the improbably great strength of 12 gram-molecules per litre will not be precipitated at all by this mixture of ammonium chloride and ammonia, and also that magnesium hydroxide will dissolve in it.

In the same way the sulphide of, say, zinc will dissolve in a mixture of hydrogen sulphide and hydrogen chloride.

Ions may also be removed from solution by combination with substances in solution to form *complex ions*. The addition, therefore, of a substance which combines with an ion yielded by a sparingly soluble substance will cause that substance to dissolve.

Consider the example of silver chloride, which is well known to be soluble in ammonia. Silver chloride is very slightly soluble in water. Thus solid silver chloride is in equilibrium with the silver ions and chloride ions formed by its dissociation.

$$\underset{\text{Solid.}}{AgCl} \rightleftharpoons Ag^+ + Cl^-.$$

Silver ion combines with ammonia, forming an argentammonium ion $Ag(NH_3)_2^+$,

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+,$$

and the equilibrium is such that nearly all the silver ion will combine with the ammonia, and so be removed from solution.

It will follow, then, that to restore the concentration of silver ion, more silver chloride will dissolve, and the process continues until all the silver chloride has dissolved or until the argentammonium ion has accumulated in quantity sufficient to be in equilibrium with enough silver ion to reach the solubility product of silver chloride.

Ammonia, the cyanide ion and the nitrite ion are particularly prone to form complex ions. Some of these are in equilibrium with an appreciable quantity of the metallic ion, as for example, the cadmicyanide ion $Cd(CN)_4^{--}$, while others such as the cuprocyanide ion $Cu_2(CN)_8^{====}$ and the argentammonium ion remove the metallic ion almost completely.

The formation of complex ions is a common phenomenon and many apparently anomalous solubility relationships are explained by it.

**121. Hydrolysis.**—Water has a decided effect upon the salts of weak acids and of weak bases.

Water is slightly dissociated,

$$H_2O \rightleftharpoons H^+ + OH^-,$$

and it is found that the product of the concentrations of these ions is nearly equal to $10^{-14}$.

$$[H^+][OH^-] = 10^{-14}.$$

A salt AB in solution contains the ions $A^+$ and $B^-$, basic and acid ion. The former of these will be in equilibrium with any hydroxyl ion present, and the latter with any hydrogen ion,

$$A^+ + OH^- \rightleftharpoons AOH,$$
$$B^- + H^+ \rightleftharpoons HB.$$

If, however, AOH or HB is a weak acid or base, *i.e.*, slightly dissociated, the hydrion or hydroxyl ion resulting from the water will be in equilibrium with a much larger quantity of the free acid or base. If, however, AOH or HB is a strong base or acid it will not be formed, for strong acids and bases are completely dissociated. Thus a salt of a strong base and weak acid will contain the free acid. The removal of hydrion to form the free acid will cause the hydroxyl ion of the water to accumulate, and the solution will have an alkaline reaction.

Thus (1) *a solution of a salt of a weak acid and strong base is alkaline and contains the free acid.*

(2) *A solution of a salt of a strong acid and weak base is acid, and contains the free base.*

(3) *A solution of a salt of a weak acid and weak base may be either acid, alkaline or neutral, and contains both free acid and free base.*

An example of the first case is sodium cyanide, of the second case ferric chloride, of the third case aluminium acetate.

The measurement of the degree of hydrolysis can be performed by determining the equilibrium constant by the partition coefficient method, the use of conductivity measurements, etc.

**122. Buffer Salts.**—A 'buffered' solution is one of which the acidity or alkalinity (*i.e.*, concentration of hydrion or hydroxyl ion) remains nearly constant despite the addition of comparatively large amounts of acid or alkali. This condition is attained by adding to it large quantities of a salt of a weak acid and strong base. Consider a solution containing in one litre 5 gram-molecules of sodium acetate. The concentration of acetanion will be perhaps 2 gm.-mols. per litre. The dissociation constant of acetic acid is $1{\cdot}8 \times 10^{-5}$, and so

$$\frac{[H^+][C_2H_3O_2^-]}{[C_2H_4O_2]} = 1{\cdot}8 \times 10^{-5},$$

or

$$\frac{[H^+] \times 2}{[C_2H_4O_2]} = 1{\cdot}8 \times 10^{-5}.$$

Suppose now that 100 c.c. of strong hydrochloric acid are added. This adds to the solution 1 gm.-mol. hydrion. Of this hydrion some, say $x$ gm.-mols., will combine with the acetanion, forming $x$ gm.-mols. of acetic acid and leaving $h$ gm.-mols. of hydrion free.

We then have two equations :

$$\frac{h.(2-x)}{x} = 1{\cdot}8 \times 10^{-5}.$$

$$1 - h = x.$$

Solving these we obtain $h = \cdot 00018$ gm.-mols. p.l.

Thus the addition of 100 c.c. of strong hydrochloric acid makes the solution only just acid.

Suppose the 100 c.c. of hydrochloric acid had been added to a little plain water. Since concentrated hydrochloric acid is just over ten times normal and is completely dissociated when diluted, we should have obtained a roughly normal solution of hydrion (1 gm.-mol. per litre). The presence of sodium acetate thus reduces the concentration of the hydrion about sixty thousand times. Sodium phosphate is also much employed for this purpose.

Buffered solutions find a use in physiological work and also in analysis, in cases where a solution has to be kept at a constant and low hydrogen ion concentration.

**123. The Voltaic Battery.**—It has been known since 1800 that when two plates, made of dissimilar metals, are immersed in a solution of an electrolyte an electric current flows along the wire connecting them. The ordinary voltaic cell consists of plates of copper and zinc immersed in dilute sulphuric acid. Using the ordinary electrical terminology we may say that a current flows from the copper to the zinc along a wire connecting the plates, though in fact the negatively-charged electrons flow from the zinc to the copper. While the current is flowing the zinc dissolves in the acid, forming zinc sulphate (*i.e.*, zinc ion, $Zn^{++}$). Hydrogen appears on the *copper* plate, which is not attacked by the acid. The deposition of this film of hydrogen soon 'polarises' the cell, stopping the action by changing the character of the surface of the copper. The explanation of the action of the cell is that the zinc goes into solution as zinc ion. Zinc ion, $Zn^{++}$, has two negative electrons less than metallic zinc, and when it is formed these electrons lost by the zinc are conducted through the zinc and the wire to the copper. At the copper surface they combine with the hydrion of the acid, forming hydrogen gas.

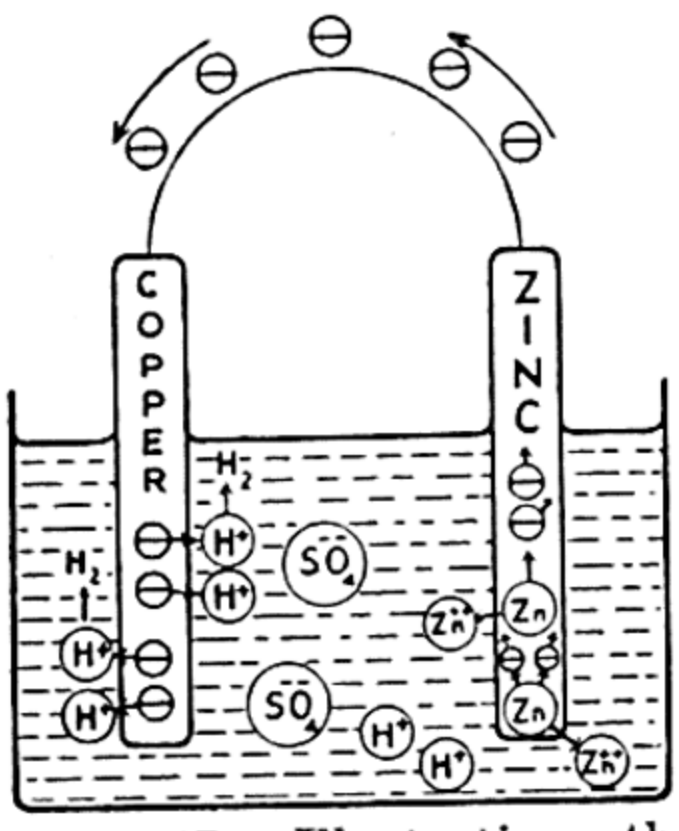


FIG. 47.—Illustrating the principle of the voltaic battery.

The explanation accounts for the formation of the current; the value of the E.M.F., produced by the battery depends on other factors, in chief, the nature of the metals concerned.

**124. Other Batteries.**—The voltaic cell is not of practical use, for polarisation within a few seconds diminishes the current to a negligible quantity. Most practical forms of cell are designed to avoid this trouble. The commonest method of avoiding it is to use a positive

pole of carbon, which is not easily oxidised, and to surround this with an oxidising agent, which removes the hydrogen as soon as formed. Thus the *bichromate* cell employs an electrolyte of potassium bichromate and sulphuric acid. Many cells, among which is notable the *Daniell* cell, employ two liquids. This cell has a negative plate of zinc in dilute sulphuric acid separated by a porous pot from a saturated solution of copper sulphate. The positive plate is a sheet of copper. The zinc dissolves, forming electrons (as in the voltaic cell) which flow to the copper. But here, instead of combining with hydrion to form the polarising hydrogen, they unite with the copper ion of the copper sulphate,

$$Cu^{++} + 2\ominus = Cu,$$

forming copper, which deposits on the plate without altering its electrical properties.

The most important cell from the commercial point of view is the Leclanché type, which includes the dry batteries, the manufacture of which is now a very considerable industry. A common type is illustrated in Fig. 48. A zinc case, E, acts as negative pole. Within this is a layer of absorbent cardboard, D, saturated with ammonium chloride solution, and within this is a bag, C, containing a moist mixture, A, of carbon, manganese dioxide, ammonium chloride and zinc chloride. Within this is set the carbon positive pole.

The zinc forms zinc ion and liberates electrons as in the voltaic cell.

$$Zn = Zn^{++} + 2\ominus.$$

These travel to the carbon and meet the positive ammonium ion

$$2\ominus + 2NH_4^+ = 2NH_3 + 2H.$$

thus forming ammonia and hydrogen. The former remains dissolved but the latter reacts with the manganese dioxide and is oxidised to water,

$$2H + 2MnO_2 = H_2O + Mn_2O_3.$$

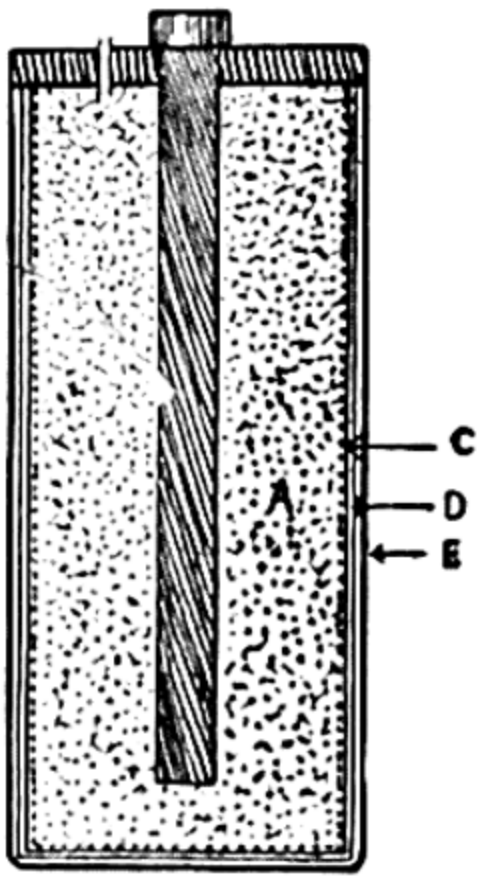


FIG. 48.—Dry cell, Leclanché pattern.

The cell polarises temporarily if too great an output is demanded, but will yield small currents for an indefinite period.

**125. Electromotive Force and Chemical Affinity.**—By the chemical affinity between two substances is meant the tendency of these substances to react. If we say that chlorine has greater affinity for zinc than for copper, we mean that chlorine tends to combine more readily and more vigorously with the former than with the latter.

How are we to measure or estimate the degree of this chemical affinity? The tendency of any process to take place runs roughly parallel with the energy change which occurs at the same time. Thus the difference of energy between a mass of zinc and chlorine and the same mass of these elements combined as zinc chloride gives a measure of the affinity of chlorine for zinc. This difference of energy was at one time taken to be equal to the heat given out in the process, but it is now recognised that the internal energy of the compound formed may account for a part of the energy difference. None the less, the heat of reaction between two chemical substances which react with liberation of a good deal of energy does, in fact, afford a rough measure of their chemical affinity. Thus we find that one gram-molecule of zinc (65 gms.) combines with one gram-molecule of chlorine (71 gms.), liberating about 97,300 cals., while the combination of one gram-molecule of copper (63·5 gms.) with one gram-molecule of chlorine liberates only about 51,500 cals.

These facts would lead us to suppose that chlorine has a greater affinity for zinc than for copper.

We have, moreover, two other methods of estimating chemical affinity.

If chlorine combines less firmly with copper than with zinc, it should be found that zinc will *displace* copper from its compound with chlorine and liberate energy in so doing, provided, of course, that other factors besides the affinity of the elements do not hinder the reaction. If we immerse a piece of zinc in a solution of copper chloride we find that a reaction takes place, that heat is liberated and zinc dissolves, forming zinc chloride, while copper is deposited.

The course of this chemical reaction then confirms our view that heat of reaction is a measure of chemicalaffinity.

When a compound is formed in a voltaic cell (§ 123) electrical energy is produced. The *quantity* of electricity produced depends on the number of atoms of the element converted into its compound, but the *potential* of the electricity depends on the work done in building up the compound formed in the cell. For suppose C faradays of electricity to be produced when $w$ gms. of a compound are formed in a cell, then by Faraday's laws

$$\frac{w}{\text{electro-chemical equivalent}} = \text{C}.$$

If the difference of potential is E then the work done by the current will be EC. Now the chemical affinity represents the work given out in building up 1 gm. of the compound from its elements, say W, then $w$W units of work will be given out in building up $w$ gms. Since the formation of the compounds is the source of the electrical work

$$w\text{W} = \text{EC}$$

but $$w = e\text{C}$$

$\therefore$ $$\text{W}e = \text{E}.$$



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W = affinity per gram of compound formed.
We = affinity per gram equivalent of component.

∴ E, the difference of potential produced, is the measure of the chemical affinity of the reaction in question.

It follows then that we can use the E.M.F. produced when an element forms a compound as a measure of chemical affinity.

**126. Electrochemical Series of the Elements.**—If we arrange a number of simple voltaic cells by placing a plate of a metal and a plate of another metal (say copper) in a solution of, say, 1/10N sulphuric acid we shall find that the electromotive force given by this arrangement varies according to the metal used. Thus, zinc and copper give a voltage of about + 1·1 volts, while iron and copper give about + 0·67 volt, and mercury and copper give a voltage of − 0·4 (*i.e.*, an E.M.F. of 0·4 volt acting in the opposite direction). By measurements of this kind we can construct a table of the elements in which any element (*a*) which is higher than another (*b*) in the table will give a greater E.M.F.[1] than the lower when both are used in separate but similar voltaic cells together with the same metal (*c*) for the other plate.

The series built up in this way should represent the relative chemical affinities of the elements comprised in it. If we construct a table so arranged that any element in it will displace any element below it from combination, we obtain a table practically identical with the electromotive-force series we have just described. Difficulties in constructing these displacement tables are brought about by the influence of other factors than the affinity of the elements concerned, but the table as printed represents very closely both the chemical affinity and the electrical behaviour of the elements. The difficulty of constructing such a table on the basis of displacement is occasioned chiefly by the fact that the concentration of the displaced ion varies while displacement is going on, falling to zero when displacement is complete. The potential differences on which the electrical series is based are calculated on the basis of a normal solution of the ion.

The further apart are any two elements in the table :

(1) The greater the E.M.F. produced when they form the plates of a voltaic cell.

(2) The more readily the upper element will displace the lower from its compounds. (Where elements are very close such displacement may not occur.)

(3) The greater the heat of combination between such elements (if they combine).

[1] Reckoned as acting in the external circuit *from* the element *a* or *b* to the element *c*.

**Electropositive.**

Cæsium.
Rubidium.
Potassium.
Sodium.
Lithium.
Barium.
Strontium.
Calcium.
Magnesium.
Aluminium.
Chromium.
Manganese.
Zinc.
Cadmium.
Iron.
Cobalt.
Nickel.
Tin.
Lead.
Hydrogen.
Antimony.
Bismuth.
Arsenic.
Copper.
Mercury.
Silver.
Palladium.
Platinum.
Gold.
Iridium.
Rhodium.
Osmium.
Silicon.
Carbon.
Boron.
Nitrogen.
Selenium.
Phosphorus.
Sulphur.
Iodine.
Bromine.
Chlorine.
Oxygen.
Fluorine.

**Electronegative.**

The chemical behaviour of the metals is represented very clearly by their position in the table. A table of the commoner metals printed below, showing the connection between their chemical properties and their position affords one of the best ways of remembering their properties. It will be seen that the grouping of the metals according to their chemical behaviour agrees very closely with their grouping according to chemical affinity. It should be remembered that some of the horizontal dividing lines should not be interpreted too literally, *e.g.*, the ' insoluble ' hydroxides are not to be taken as wholly insoluble. The table gives a good basis of fact but cannot be taken as holding good under all conditions.

| | Combustion. | Action on water. | Action on acids. | Reduction of oxides. | Action of heat on oxides. | Action of water on oxides. | Character of hydroxides. | Solubility of certain salts. | Action of heat on nitrates. |
|---|---|---|---|---|---|---|---|---|---|
| Potassium, Sodium | Burn in air or oxygen readily. | Decompose cold water. | Attacked by dilute acids. | Oxides not reduced by hydrogen. | Oxides stable when heated. | Oxides react with water to form hydroxide. | Hydroxides appreciably soluble in water "alkalis." | Phosphate silicate carbonates, etc. soluble in water. | Nitrates decompose to nitrite when heated. |
| Barium, Strontium, Calcium, Magnesium, Aluminium[1], Chromium[1], Manganese, Zinc, Cadmium, Iron, Cobalt, Nickel, Tin, Lead, Antimony, Copper, Mercury, Silver | | Decompose steam at a red heat or a little above. | | | | | | | Nitrates decompose to oxide. |
| | Oxidise when heated in air. | Decompose steam at a white heat. | Attacked only by oxidising acids. | Oxides reduced by hydrogen. | Oxides decomposed when heated. | Oxides do not react with water. | Hydroxides insoluble. | Carbonates insoluble in water. | |
| Platinum, Gold | Unaffected by oxygen. | Do not decompose water or steam at all. | Not attacked by acids. | | | | Hydroxides not formed. | | Nitrates decompose to metal. |

[1] These elements do not conform to the whole table as given unless the resistant film of oxide which normally coats their surface is removed.

## CHAPTER VII

# VALENCY, THE PERIODIC TABLE AND THE STRUCTURE OF THE ATOM

**127. The Atom in the Nineteenth Century.**—The Atomic Theory put forward by Dalton in 1808 was so valuable in explaining the chemical behaviour of substances, and the Kinetic Theory was found so valuable an assumption in physics, that the atomic nature of matter was not seriously doubted during the nineteenth century. None the less, practically nothing was known about the size, etc., of the atom until the last decade of that century; and until 1897 there was no evidence that the atom had any structure at all and was in any respect other than a "hard massy particle."

The one property which clearly belonged to the actual atom itself and not to an assemblage of atoms was its combining power or *valency*. The regularities observed in the valencies of the various elements have given rise to endless theories and discussions. There was, for a long time, so little evidence as to the real nature of valency that many chemists took up an almost mystical attitude about the subject, as if it belonged to the region of the unknowable. Two great discoveries stand as landmarks in our survey of the nature of valency and chemical combination—the Periodic Table and the Electronic Theory of Valency.

**128. Valency.**—The valency of an element is a number expressing the combining power of its atom. If we examine the formulæ of a number of compounds we note at once certain regularities. The table below shows the formulæ of the hydrides, fluorides, oxides

| Element. | Formula of Compound with | | | |
|---|---|---|---|---|
| | Hydrogen. | Fluorine. | Oxygen. | Sulphur. |
| Sodium . | $NaH$ | $NaF$ | $Na_2O$ | $Na_2S$, $Na_2S_5$ |
| Magnesium | — | $MgF_2$ | $MgO$ | $MgS$ |
| Aluminium | — | $AlF_3$ | $Al_2O_3$ | $Al_2S_3$ |
| Silicon . | $SiH_4$ | $SiF_4$ | $SiO_2$ | — |
| Phosphorus | $PH_3$ | $PF_3$, $PF_5$ | $P_2O_3$, $P_2O_4$, $P_2O_5$ | $P_2S_5$ |
| Sulphur . | $SH_2$ | $S_2F_2$, $SF_6$ | $SO_2$, $SO_3$, $S_2O_3$, $S_2O_7$ | — |
| Chlorine . | $HCl$ | $ClF$ | $Cl_2O$, $ClO_2$, $Cl_2O_7$ | $S_2Cl_2$, $SCl_4$ |
| Iron. . | — | $FeF_2$, $FeF_3$ | $FeO$, $Fe_3O_4$, $Fe_2O_3$ | $FeS$, $Fe_2S_3$, $FeS_2$ |

and sulphides of the elements sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine and iron.

It will be noticed at once that where an atom of sodium combines with $n$ atoms of another element an atom of magnesium combines with $2n$ and an atom of aluminium $3n$, and an atom of silicon $4n$ atoms.

We may express these facts by saying that each atom has a combining power or *valency*. It appears from all the hundreds of thousands of chemical formulæ hitherto studied that a single atom of hydrogen never combines with more than one atom of any other element, *i.e.*, we have compounds such as XH and $XH_n$, but never $X_nH$.[1] We therefore take the combining power of hydrogen as unity. By examination of formulæ the valencies or combining powers of all the elements are easily ascertained. Since hydrogen and fluorine have each the valency of one and since every element which forms any compound combines with one or other of these we may define the valency of an element as *the number of hydrogen or fluorine atoms with which a single atom of the element combines.*

By the application of this definition we readily ascertain at any rate some of the possible valencies of the element in question, though not necessarily all.

It will be seen from the table on p. 154 that the valency of an element is not constant in all cases. Certain elements have only one valency, *e.g.*, sodium (1), magnesium (2) and aluminium (3), while others, such as phosphorus, have two or more possible values. It is found that no element has a greater valency than eight and that the majority of elements have either one fixed valency or one valency which is more readily assumed than any other.

Valency has been for a long time regarded as behaving more like a material bond of attachment, such as a hook or string, than the influence of an immaterial force such as, say, the electrostatic attraction of an atom of an electronegative element for an atom of an electropositive element—a theory at one time widely held but dropped on account of the difficulties presented by organic compounds, in which electronegative atoms, such as those of chlorine, can *replace* electropositive atoms, such as those of hydrogen, with very little resultant change in the properties of the compound.

Chemists have for a long time pictured the valency of an atom as exerted through *valency-bonds*, which they represented pictorially by a line, and regarded as capable of linking any two atoms irrespective of their electrical character.

[1] Hydrazoic acid, $HN_3$, is an apparent exception; we shall see, however (§ 704), that the hydrogen atom is only directly combined with one of the nitrogen atoms.

Thus an atom of univalent hydrogen is represented as H —, an atom of tervalent aluminium as Al ≡ etc. It is considered that when a compound is formed the combining power of the elements is mutually satisfied and that accordingly the formula of the compound can be represented by the symbols for the constituent atoms connected by valency bonds. Thus, for example, when H — and Cl — atoms combine, the compound H — Cl has no remaining combining power.[1] A knowledge of the valency of the elements is therefore our chief and most valuable guide in the determining of the structure of compounds. Moreover, a knowledge of the valency of the elements concerned, coupled with a certain amount of knowledge as to the types of compounds commonly formed, enables the chemist to deduce the formulæ for a great many compounds, and so saves him the labour of remembering them.

Thus, if we wish to know the formula of copper sulphide we remember that copper is both univalent and bivalent, and that sulphur (in the sulphides of metals) is bivalent. There can be two copper sulphides and their formulæ will be

(*a*) Copper univalent $\begin{matrix} Cu - \\ Cu - \end{matrix}$ S, $Cu_2S$.

(*b*) Copper bivalent Cu = S, CuS.

These are the *simplest* formulæ to be predicted, but the considerations of valency do not exclude such formulæ as

$$Cu - S - S - Cu \text{ or } Cu\begin{matrix} \diagup S - S \\ \diagdown S - S \end{matrix}\Big|$$

though, in fact, these compounds do not exist.

Again, if the formula for aluminium oxide is required, the valencies of aluminium and oxygen being known to be 3 and 2 respectively, the simplest formula is seen to be O = Al — O — Al = O, $Al_2O_3$, which is correct. Again, however, $O\begin{matrix} \diagup Al \\ \| \\ \diagdown Al \end{matrix}$, $Al_2O$, is a possible formula, though in fact no such compound as $Al_2O$ exists.

It is, then, in general, true that the formulæ of the simplest compounds of two elements may be predicted from their valencies with success, but that many more compounds may be predicted than actually exist.

**129. List of the Valencies of the Elements.**—Some elements have the same valency in all of their compounds; others have two or more possible valencies.

[1] But see § 130, on co-ordinate valencies.

(1) Elements of fixed valency :—

| *Nullivalent.* | *Univalent.* | *Bivalent.* | *Tervalent.* | *Quadrivalent.* |
|---|---|---|---|---|
| Helium. | Hydrogen. | Beryllium. | Aluminium. | Hafnium. |
| Neon. | Lithium. | Magnesium. | Scandium. | Zirconium. |
| Argon. | Sodium. | Calcium. | Lanthanum. | Thorium. |
| Krypton. | Potassium. | Strontium. | Most rare-earth elements. | |
| Xenon. | Rubidium. | Barium. | | |
| Emanation. | Cæsium. | Radium. | | |
| | Fluorine. | Zinc. | | |
| | | Cadmium. | | |
| | | Mercury.[1] | | |

(2) Elements of variable valency. (Elements are in italics where they appear under the heading of a valency which they very rarely assume.)

| *Univalent.* | *Bivalent.* | *Tervalent.* | *Quadrivalent.* | *Quinquevalent.* | *Sexivalent.* | *Septivalent.* | *Octavalent.* |
|---|---|---|---|---|---|---|---|
| Copper. | Copper. | Gold. | Boron. | Nitrogen. | Sulphur. | Chlorine. | Osmium |
| Silver. | *Silver.* | Boron. | Carbon. | Phosphorus. | Selenium. | Bromine. | Ruthenium |
| Gold. | Mercury. | Indium. | Silicon. | Arsenic. | Tellurium. | Iodine. | |
| Indium. | Indium. | Thallium. | Germanium. | Antimony. | Chromium. | Manganese. | |
| Thallium. | Gallium. | Rare earths. | Tin. | Bismuth. | Molybdenum. | Rhenium. | |
| Chlorine. | Germanium. | Titanium. | Lead. | Chlorine. | Tungsten. | | |
| Bromine. | Lead. | Nitrogen. | Titanium. | Bromine. | Uranium. | | |
| Iodine. | Tin. | Phosphorus. | Sulphur. | Iodine. | Rhenium. | | |
| | *Silicon.* | Arsenic. | Tungsten. | | | | |
| | Titanium. | Antimony. | Manganese. | | | | |
| | Oxygen. | Bismuth. | Rhenium. | | | | |
| | Sulphur. | Chromium. | Uranium. | | | | |
| | Selenium. | Molybdenum. | | | | | |
| | Tellurium. | Tungsten. | | | | | |
| | Chromium. | Manganese. | | | | | |
| | Manganese. | Iron. | | | | | |
| | Iron. | Iodine. | | | | | |
| | Nickel. | *Carbon.* | | | | | |
| | Cobalt. | | | | | | |

Some regularities were early noticed in these lists, such as the fact that elements which were physically and chemically similar usually had the same valency, but it was the introduction of Mendeléeff's Periodic Table which first brought out the regularities and peculiarities of the distribution of valencies.

**130. Types of Valency Linkage.**—There are two very definitely different kinds of valency linkage between the parts of a compound, corresponding to the two distinctive types of compound.

(1) *Electrovalency.*—This type of connection joins the ions or radicals of alkalis or salts. These linkages are distinguished by their *polar* character, by which we mean that they bind together two atoms or radicals which possess opposite electrical charges. These linkages are also distinguished by the fact that they are broken when the compound in which they occur is dissolved in water or other ionising solvent, the parts of the compounds formerly linked becoming separate charged ions (§ 115).

Indeed, this type of connection is not a linkage at all, in the strict sense. It knits the ions into a compact crystal-array but it does not convert them into separate distinguishable molecules.

[1] See § 440.

If we wish to distinguish this type of connection symbolically we enclose one or both of the parts of the compound so linked in separate brackets. Thus we may write the formula of copper sulphate $Cu[SO_4]$, or $[Cu]^{++}[SO_4]^{--}$, implying that in solid copper sulphate equal numbers of cupric ions and sulphate ions are associated as a result of a double positive charge on the former and a double negative charge on the latter; and that when the salt is dissolved in water the solution will contain the free ions $Cu^{++}$ and $SO_4^{--}$.

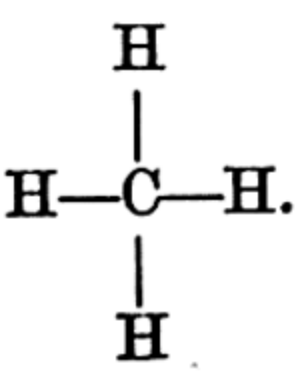
The sulphur and oxygen atoms in the $SO_4$ group are linked in a different manner. Thus sulphur and oxygen are *both* strongly electronegative and the $SO_4$ group does not break up on solution in water into sulphur and oxygen ions.

The electrovalency shown by an atom or group is never higher than 4. Thus chlorine in metallic *chlorides* is always univalent, sulphur in metallic *sulphides* is divalent, although in non-polar compounds their valencies reach 7 and 6 respectively.

(2) *Non-polar Linkages.*—These are subdivided into *covalent* and *co-ordinate* linkages.

(*a*) *Covalent Linkages.*—These are to be found in almost all types of compound. The great majority of organic compounds, and all inorganic compounds which are not electrolytes (*e.g.*, carbon monoxide, nitrous oxide, ammonia) are bound by these linkages only, while such compounds as sodium sulphate $Na_2SO_4$, ammonium chloride $NH_4Cl$, etc., contain both types.

These non-polar linkages do not necessarily connect atoms of opposite electrical polarity and they do not undergo ionisation. Higher valencies may be exhibited in covalent linkages than in polar or ionisable linkages. Covalent linkages are represented by a line —, as



Certain compounds can exist both in covalent and electrovalent states. Thus hydrogen chloride HCl is covalent as a gas, but ionises in solution.

(*b*) *Co-ordinate Linkages.*—It is well known that apparently saturated compounds often unite to form well-marked compounds; some comparatively unstable, such as

$$CuSO_4 . 5H_2O,\ CaCl_2 . 6NH_3, \text{ etc.},$$

others quite stable, such as the metallic ammines, pp. 794 ff.

The linkage in these compounds is distinguished by its power of uniting apparently saturated compounds, and by the fact that the number of such linkages often appears to have no connection with the valency of the elements concerned as indicated by the periodic table. Such linkages are denoted symbolically by an arrow → the exact significance of which will appear at a later stage (§ 155).

These three types of valency could receive little in the way of explanation until an adequate theory of the structure of the atom had been put forward, and after a short exposition of this theory it will be possible to give an adequate, though not complete, explanation of the nature of valency and chemical combination.

## The Periodic Table

**131. The Evolution of the Periodic Table.**—The chemical elements were at first thought to be separate and unrelated primary substances. A few likenesses were noted, such as those of sodium and potassium ; calcium, strontium and barium, etc. ; and Döbereiner, in 1829, noted that the atomic weights of such related elements varied in a regular manner as

| | | Difference. |
|---|---|---|
| Calcium . . . | 40 | 47 |
| Strontium . . . | 87 | 50 |
| Barium . . . | 137 | |

Newlands, in 1864, went further and attempted to classify the elements in ' octaves,' according to their order of atomic weight, as was later done in the periodic table. Newlands showed that in such a list every eighth element resembled the element eight places before it ; but since atomic weights of adequate accuracy were not available his evidence was not sufficiently compelling and he met with some ridicule, a member of a learned society inquiring whether he had thought of classifying the elements according to their initial letters.

Mendeléeff, in 1869, discovered that if the elements were placed in a list in order of their atomic weights, there was a recurrence of similar properties at regular intervals, and that consequently a table could be constructed in which the elements were arranged horizontally in order of atomic weight and vertically according to their likeness in chemical properties.

Mendeléeff's original table is not quite so clear in its arrangement as some more modern forms, and the form of table given on pp. 158–159 shows Mendeléeff's original scheme as modified to conform with modern knowledge. Many other arrangements have been made

on similar principles, but the table given has the advantage of representing the relationships adequately without departing too far from the traditional form.

**132. General Structure of the Periodic Table.**—Beginning with hydrogen, the element of lowest atomic weight, we place the elements in order of their atomic weights as we pass successively from left to right, commencing a new 'period' of elements at intervals of 2, 8, 8, 18, 18, and 32 elements respectively. When this is done we find that the elements are arranged vertically in 'families' or 'groups' each of which contains elements of like chemical properties. The groups numbered VIII. and 0 are peculiar in that they are alternatives. An element of Group VII. A is always followed by three elements closely resembling both it and each other and the succeeding element of Group I. B. Thus manganese (VII. A) is followed by iron, cobalt and nickel (VIII.), providing a steady transition to copper (I. B). An element of Group VII. B, which contains the strongly electronegative halogens, is followed, on the contrary, by an element of Group 0, having no chemical properties, which is again followed by an intensely electropositive element of Group I. A (the alkali metals).

An exception to the general plan is made in the case of the 'rare-earth' elements, Nos. 57–71, which are all placed in the same group of the periodic table. This procedure is indicated by their extreme likeness to one another and also by their peculiar type of atomic structure (§ 506).

A few elements have had to be displaced from their natural order to make the table correspond adequately with the chemical properties of these elements. Thus argon, 39·9, precedes potassium, 39·1, instead of following it, while iodine, 126·92, follows tellurium, 127·5. This procedure has been fully justified by the discovery of isotopes (§ 148).

**133. The Short and Long Periods.**—*Period* 1.—The first period consists of two elements, hydrogen and helium. Hydrogen being univalent and electropositive is usually placed with the alkali-metals. It has, however, certain resemblances to the halogens and has sometimes been placed with them. It is probably best not to assign hydrogen to any family, for its atomic structure is fundamentally different from that of any other element. Our present knowledge of atomic structure indicates that there can be no elements between hydrogen and helium.

*Periods* 2 and 3.—The second and third periods both consist of eight elements, which we place in groups which we number I.–VIII. The elements which fall into these groups have the same valency and a close chemical resemblance. At this point we may mention the

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## Periodic Table

### Atomic Numbers thus, 7.

| Group | I. A. | I. B. | II. A. | II. B. | III. A. | III. B. | IV. A. | IV. B. | V. A. | V. B. |
|---|---|---|---|---|---|---|---|---|---|---|
| Period 1 | Hydrogen, H. 1. *1·008.* | | | | | | | | | |
| ,, 2 | Lithium, Li. 3. *6·94.* | | Beryl-lium Be. 4. *9·0.* | | Boron, B. 5. *10·8.* | | Carbon, C. 6. *12·00.* | | Nitrogen, N. 7. *14·01.* | |
| ,, 3 | Sodium, Na. 11. *23·00.* | | Magnesium, Mg. 12. *24·32.* | | Aluminium, Al. 13. *26·97.* | | Silicon, Si. 14. *28·06.* | | Phosphorus, P. 15. *31·02.* | |
| ,, 4 | Potassium, K. 19. *39·10.* | Copper, Cu. 29. *63·57.* | Calcium, Ca. 20. *40·08.* | Zinc. Zn. 30. *65·38.* | Scandium, Sc. 21. *45·1.* | Gallium, Ga. 31. *69·72.* | Titanium, Ti. 22. *47·9.* | Germanium, Ge. 32. *72·6.* | Vanadium, V. 23. *50·95.* | Arsenic, As. 33. *74·93.* |
| ,, 5 | Rubidium Rb. 37. *85·44.* | Silver, Ag. 47. *107·88.* | Strontium, Sr. 38. *87·63.* | Cadmium, Cd. 48. *112·41.* | Yttrium, Yt. 39. *88·92.* | Indium, In. 49. *114·8.* | Zirconium, Zr. 40. *91·2.* | Tin, Sn. 50. *118·7.* | Niobium, Nb. 41. *93·3.* | Antimony, Sb. 51. *121·76.* |
| ,, 6 | Cæsium, Cs. 55. *132·91.* | Gold, Au. 79. *197·2.* | Barium, Ba. 56. *137·36.* | Mercury, Hg. 80. *200·61.* | Lanthanum, La. 57. *138·9.* Cerium, Ce. 58. *140·13.* Praseodymium, Pr. 59. *140·92.* Neodymium, Nd. 60 *144·27.* Promethium 61. *147.* Samarium, Sm. 62. *150·43.* Europium, Eu. 63. *152·0.* Gadolinium, Gd. 64. *157·3.* Terbium, Tb. 65. *159·2.* Dysprosium, Ds. 66. *162·46.* Holmium, Ho. 67. *163·5.* Erbium, Er. 68. *167·64.* Thulium, Tm. 69. *169·4.* Ytterbium, Yb. 70. *173·04.* Lutecium, Lu. 71. *175·0* Thallium, Tl. 81. *204·39.* | | Hafnium, Hf. 72. *178·6.* Lead· Pb. 82. *207·22.* | | Tantalum, Ta. 73. *181·4.* Bismuth, Bi 83. *209·0.* |
| ,, 7 | Francium, 87. *223.* | | Radium, Ra. 88. *225·97.* | | Actinium, Ac. 89. | | Thorium, Th. 90. *232·12.* | | Protoacti-nium, Pa. 91. | |

OF THE ELEMENTS

Atomic Weights thus, *6·94*.

| VI. A. | VI. B. | VII. A. | VII. B. | VIII. | | | 0. |
|---|---|---|---|---|---|---|---|
| | | [Hydrogen, H. 1. *1·008.*] | | | | | Helium, He. 2. *4·00.* |
| Oxygen, O. 8. *16·00.* | | Fluorine, F. 9. *19·0.* | | | | | Neon, Ne. 10. *20·2.* |
| Sulphur, S. 16. *32·06.* | | Chlorine, Cl. 17. *35·46.* | | | | | Argon, A. 18. *39·94* |
| Chromium, Cr. 24. *52·0.* | Selenium, Se. 34. *79·92.* | Manganese, Mn. 25. *54·93.* | Bromine, Br. 35. *79·92.* | Iron, Fe. 26. *55·84.* | Cobalt, Co. 27. *58·94.* | Nickel, Ni, 28. *58·69.* | Krypton, Kr. 36. *82·9.* |
| Molybdenum, Mo. 42. *96·0.* | Tellurium, Te. 52. *127·6.* | Technetium, Tc. 43 *96·99.* | Iodine, I. 53. *126·92.* | Ruthenium, Ru. 44. *101·7.* | Rhodium, Rn. 45. *102·9.* | Palladium, Pd. 46. *106·7.* | Xenon, Xc. 54. *131·3.* |
| Tungsten, W. 74. *184·0.* | Polonium, Po. 84. | Rhenium, Re. 75. *186·31.* | Astatine, At. 85. *211·218.* | Osmium, Os. 76. *191·5.* | Iridium, Ir. 77. *193·1.* | Platinum, Pt. 78. *195·23.* | Emanation, Em. 86. *222·0.* |
| Uranium, U. 92. *238·14.* | | Neptunium, Np. 93. *239.* | | Plutonium, Pu. 94. *239·14.* | Americium. 95. *241.* | Curium. 96. *242.* | |

*These all form a part of group VI A.*

remarkable connection between the valency of an element and its position. **The valency of an element is in general the same as the number of its group in the periodic table, and in the case of Groups V., VI., VII. is also equal to the difference between this number and eight.**

| Group | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | 0. |
|---|---|---|---|---|---|---|---|---|---|
| Valency in hydrides and electrovalent compounds . | 1 | 2 | 3 | 4 | 3 | 2 | 1 | VARIABLE | 0 |
| Valency in oxides and covalent compounds . | 1 | 2 | 3 | 4 | 5 | 6 | 7 | VARIABLE | 0 |

Thus potassium has valency 1 ; magnesium, valency 2 ; aluminium, valency 3 ; carbon, valency 4 ; phosphorus, valency 3 in some compounds, 5 in others ; sulphur, valency 2 in hydrogen sulphide and metallic sulphides, but 6 in sulphur hexafluoride, sulphates, etc. ; chlorine, 1 in hydrogen chloride, and metallic chlorides, but 7 in the perchlorates. The above figures are characteristic of the groups, but additional values may be found, particularly among the 'transition' elements, *i.e.*, those of sub-groups IV. A, V. A, VI. A, VII. A, VIII., I. B. (§ 134).

*Periods* 4 and 5.—Starting at potassium, 18 elements, instead of 8, are met with before the next alkali metal, rubidium, is reached. Of these, the ten elements scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, are of a new type not met with before, and may be regarded as *related to* the elements of the same group in the earlier periods, but somewhat diverging from them in properties. These elements are placed in separate sub-groups ; three of them, iron, cobalt, nickel, being placed in a group by themselves as having too great a likeness to justify classification in separate families. Thus, the transition elements of the long periods are *interposed* into the eight normal elements resembling those of the earlier periods. Thus, if we disregard the transition elements for the moment we have the sequence

K . Ca . Ga . Ge . As . Se . Br . Kr,

which is closely analogous to the third short period,

Na . Mg . Al . Si . P . S . Cl . A .

Starting again from rubidium, an identical sequence is met with. The relationship between the groups, periods, transition elements and rare earths is brought out in a form of a table (Fig. 49) due to Julius Thomsen, and used by Bohr, whose work has elucidated the meaning of the Periodic Table in such a remarkable manner.

*Period* 6.—The sixth period starts like the last with two normal elements and one transition element, Cs, Ba, La resembling K, Ca, Sc respectively ; but then follows a remarkable series of fourteen elements quite distinct from one another, but of remarkably similar chemical properties. These can only be fitted into the table if they are all placed in the same group in the same manner as are iron,

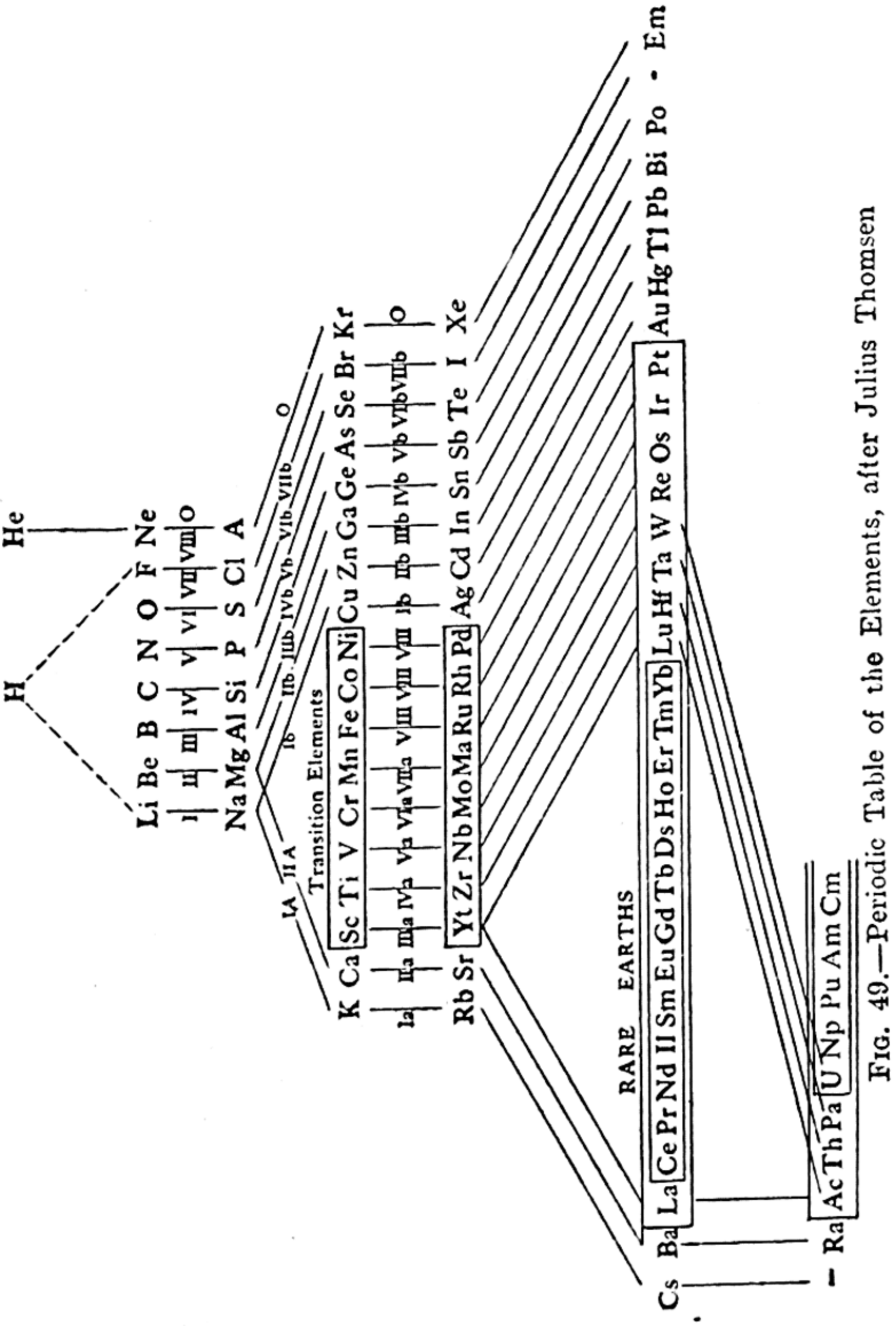


FIG. 49.—Periodic Table of the Elements, after Julius Thomsen

cobalt and nickel, the platinum metals, etc. They are tabulated vertically on pp. 154–155 for convenience in printing. The period then follows on in just the same way as the long periods 4 and 5.

*Period* 7.—This period starts like a long period, such as 5, but soon comes to an end ; for uranium, occupying the sixth space, is followed

by the four artificial elements neptunium, plutonium, americium and curium, which last has at present the highest known atomic weight. Uranium is decomposing radioactively (§ 141), one half of any quantity disappearing in 8,000,000,000 years. This period of time is so great that it seems unnecessary to assume that uranium has been formed. These four elements (§ 1271) much resemble uranium and it is probable that with uranium a group like the rare-earths begins.

**134. The Groups and Sub-Groups of Elements.**—The vertical columns into which the elements fall according to the periodic table are called *groups*. Each group (except VIII.) consists of two typical elements of the first three short periods, and thereafter two sets of elements each bearing some resemblance to those of the first three periods. As a rule one set of these resembles the earlier elements more closely than the other. The elements occurring in the first part of a long period are called the A sub-group, those in the second part the B sub-group.

As examples we may take Group I. and Group V.

| | GROUP I. | | | GROUP V. | |
|---|---|---|---|---|---|
| | A. | B. | | A. | B. |
| Main Group. | Lithium. | | Elements of short periods. | | Nitrogen |
| | Sodium. | | | | Phosphorus |
| | Potassium. | | | Vanadium. | |
| | Rubidium. | Copper | Transition elements. | Niobium. | Arsenic. |
| | Cæsium. | Silver | | Tantalum. | Antimony. |
| | —— | Gold | | Protoactinium. | Bismuth |

The B elements of Group I resemble each other closely, but have little likeness to the A elements. In Group V. the same phenomenon is found, but the transition elements in this case fall into the A sub-group. It will be seen on reference to pp. 158–159 and Fig. 49 that the 'transition elements' constitute the B sub-group in Groups I., II., but the A sub-group in Groups III., IV., V., VI., VII. The elements of the short periods resemble the sub-group which does not contain the transition elements.

The actual degree of likeness between the elements of a group varies considerably. It is always quite unmistakable as between members of a sub-group A or B individually, but it is often the case that the A and B sub-groups have only a few minor points of resemblance.

It is to be noticed that at the right-hand and left-hand extremes of the table the likeness between the A and B sub-groups is much less marked than in the middle (*e.g.*, compare Groups I. and IV.).

The resemblance between the first and second member of the Group is always less close than that between succeeding members. Thus, oxygen (Group VI. B) is less like sulphur than sulphur is like

selenium ; and fluorine is less like chlorine than chlorine is like bromine.

The system of groups affords by far the best way of classifying the elements. It is often possible to save much labour of memory by remembering the general properties of the group and the few divergencies of individual elements rather than by memorising the properties of each individual element.

**135. Gaps in the Periodic Table.**—When Mendeléeff first drew up his periodic table he had to introduce a number of blank spaces in order that the elements should fall into their proper groups as indicated by their chemical properties.

Mendeléeff predicted that the spaces left in this way would be filled by the discovery of new elements. He saw also that there was in general a gradation of properties in the groups (vertical columns) of the periodic table and that the properties of an element were, as a rule, intermediate between those of the elements immediately above it and below it. Mendeléeff accordingly gave to each of the elements which he expected to be discovered, a provisional name, compounded from that of the element immediately above it, which the new element was likely to resemble, and a Sanskrit numeral, (*eka*, *dwi*, *tri*), indicating the number of the spaces in the Table below the known element from which it was named. He predicted the properties of many of these hypothetical elements, and his predictions were, in most cases, fulfilled with remarkable accuracy. Mendeléeff predicted the discovery of ten elements in all, seven of which have been since discovered. These are indicated in the table below with their present names :—

| Mendeléeff's Prediction. | Modern Name. |
|---|---|
| Eka-aluminium . . . . | Gallium. |
| Eka-silicon . . . . | Germanium. |
| Eka-boron . . . . | Scandium. |
| Eka-cæsium . . . . | Probably do not exist. |
| Dwi-cæsium . . . . | |
| Eka-niobium . . . . | Modern tables indicate no gap. |
| Eka-tantalum . . . . | Proto-actinium. |
| Dwi-tellurium . . . . | Polonium. |
| Eka-manganese . . . . | Technetium. |
| Dwi-manganese . . . . | Rhenium. |

As an example we may place his prediction of the properties of *eka-silicon* in opposition to the actual properties of the element *germanium*, which was later discovered and was found to occupy the position in the periodic table corresponding to *eka-silicon*. The

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remarkable fulfilment of these predictions afforded the strongest evidence of the value of the periodic table and directed considerable attention to it.

| | Eka-silicon, Es. *Predictions of Mendeléeff.* | Germanium, Ge. *Actual Properties.* |
|---|---|---|
| Atomic weight | 72 | 72·60 |
| Specific gravity | 5·5 | 5·35 |
| Colour . . | Dirty grey. | Greyish-white. |
| Action of air . | Will give a white powder of the oxide, $EsO_2$, on calcination in air. | Gives the oxide, $GeO_2$, as a white powder on calcination in air. |
| Action of water | Element will decompose steam with difficulty. | The element does not decompose water. |
| Action of acids | Slight. | Not attacked by hydrochloric acid, but is attacked by aqua regia. |
| Alkalis . . | No marked action. | Solutions of caustic potash do not affect it, but it is oxidised by fused caustic alkalis. |
| Preparation . | The action of sodium on $EsO_2$ or $K_2EsF_6$ will give the element. | The reduction of $GeO_2$ with carbon or of $K_2GeF_6$ with sodium yields the element. |
| Properties of the oxide. | The oxide, $EsO_2$, will be refractory and will have sp. gr. 4·7. It will be less basic than $TiO_2$ or $SnO_2$, but more basic than $SiO_2$. | The oxide, $GeO_2$, is refractory. Its sp. gr. is 4·703 and its basic properties are feeble. |
| Hydroxide . | The hydroxide will be soluble in acids and the solutions so formed will readily decompose, forming a hydroxide. | Acids do not precipitate the hydroxide from dilute alkaline solutions, but from concentrated solutions acids precipitate $GeO_2$ or a hydroxide. |
| Chloride . | The chloride, $EsCl_4$, will be a liquid with b. p. $< 100°$C. and a sp. gr. of 1·9 at 0° C. | The chloride, $GeCl_4$, is a liquid of b. p. 83° C. and density 1·879. |
| Fluoride . | The fluoride, $EsF_4$, will not be gaseous. | The fluoride, $GeF_4$, is a gas. |
| Ethyl compound | Eka-silicon will form a compound, $Es(C_2H_5)_4$. boiling at 160° C. and of sp. gr. 0·96. | Germanium forms a compound, $Ge(C_2H_5)_4$. Its melting point is 90° C. and its boiling point is 163·5° C. Its sp. gr. is 0·9911. |

## THE PROPERTIES OF THE ATOM

**136. The Size and Number of Atoms.**—A large number of different methods have been applied to the measurement of the atom. An approximation was first obtained by various measurements of the thickness of films, the limiting value for which is evidently the diameter of a molecule. From soap films, films of oil on water, films of metal on electrodes, etc., it was deduced that the diameter of the various molecules measured was c. $10^{-7}$ or $10^{-8}$ cm.

The first accurate method of determining the size of the molecule was to find the number of molecules in a given volume and from this value and the mean free path given by viscosity measurements to calculate the molecular diameter. Other methods have since been developed based on X-ray and electron diffraction (*cf.* § 103).

The results obtained indicate a value of $2 \times 10^{-8}$ to $6 \times 10^{-8}$ cm. for the diameter of the smaller molecules. It is difficult to form any mental picture of these magnitudes. An idea may be gained of its size by saying that one could put as many oxygen molecules on a full-stop as one could put full-stops on Kensington Gardens (*c.* 275 acres).

**137. The Number of Molecules in a Given Volume of Gas.**—According to Avogadro's law equal volumes of gases contain equal numbers of molecules under the same conditions of temperature and pressure. It is of importance for many reasons to know the number of molecules in a gram-molecule of gas at N.T.P. (22·4 litres), which quantity is known as the Avogadro Number.

The most accurate determinations of these quantities are afforded by a study of (*a*) the "Brownian movement," and (*b*) the charge on one electron.

*Brownian Movement.*—When any suspension of very fine particles in a liquid (or gas) is examined with a microscope the particles are seen to be in continuous rapid and irregular motion. This motion never ceases and is only influenced by the size of the particles and the temperature. The smaller are the particles the more rapid their motion. Thus particles of carbon in diluted india ink show a trembling and vibratory motion, while the minute particles of colloidal gold (§ 327) are seen under the ultramicroscope to be dashing vigorously in every direction. An increase of temperature causes an increase in velocity.

The only satisfactory explanation of this movement is that it results from the bombardment of the particle by the molecules of the liquid in which it is suspended. A particle may be struck on one side by more or faster molecules than strike it on the other and the energy imparted to it will be enough to move it. A fraction of a second later the contrary effect may take place and the motion be thus reversed.

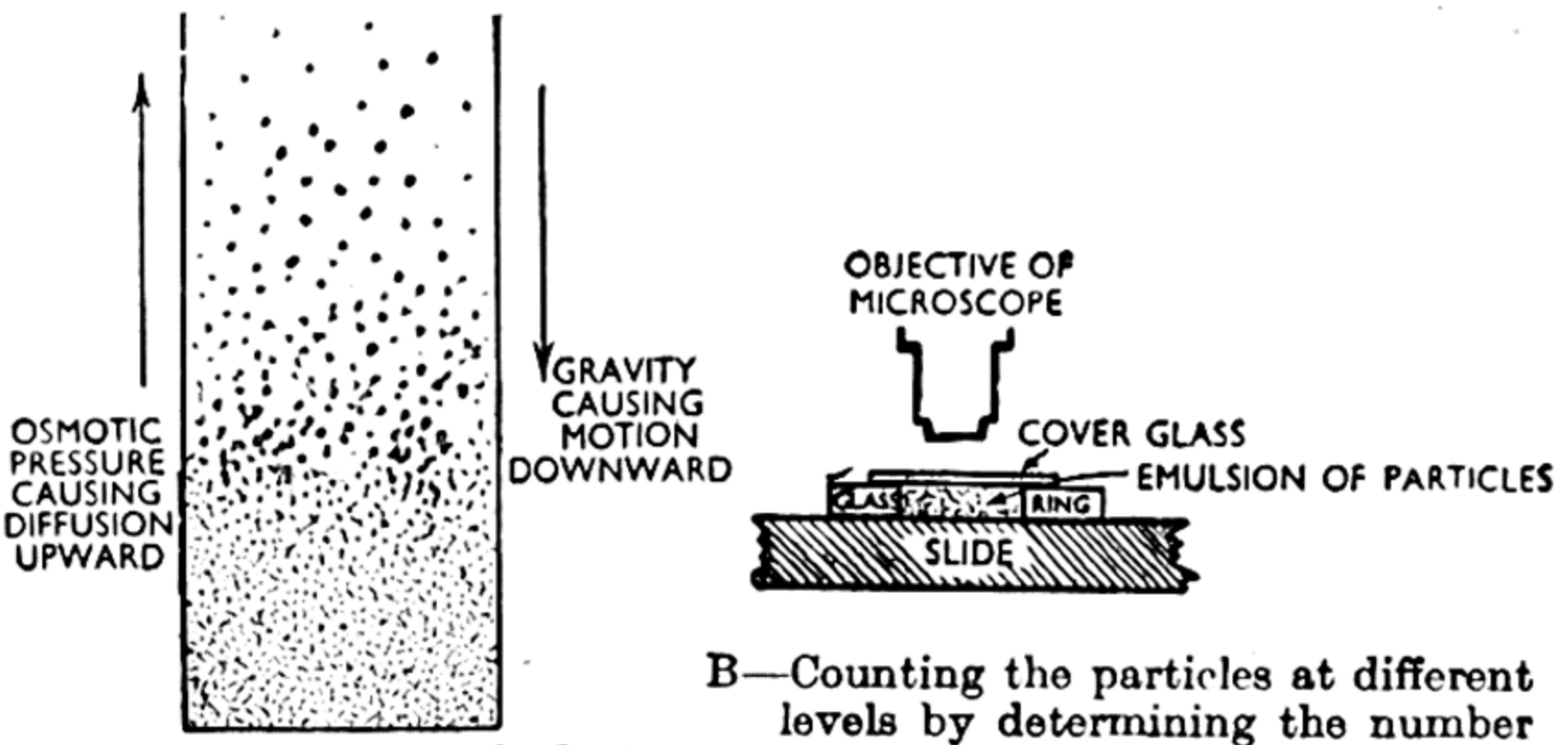
Perrin started from the fact, established by work on osmotic pressure, etc.,

that "*at the same temperature all the molecules of all fluids have the same mean kinetic energy.*"

He assumed that a particle suspended in a liquid would behave like a molecule and have the same mean kinetic energy as a molecule of the liquid. From this assumption he calculated the rate at which a suspension of such particles should thin out under the action of gravity (as the molecules of air thin out as we ascend a mountain). He obtained an equation

$$\frac{2}{3} w \log \frac{n_0}{n} = \phi (\mathrm{D} - \delta) gh,$$

where $w$ is the mean kinetic energy of the particle; $n_0$ and $n$ the average number of particles per unit volume at levels separated by a vertical interval $h$; $\phi$ the volume of a granule; D, $\delta$, the densities of granule and liquid. The right-hand expression represents the gravitational force pulling the granules down and the left-hand expression the osmotic pressure (due to kinetic motion) forcing them up. In this way, all the above values except $w$ being determinable, the mean kinetic energy of the individual particles was found. Fig. 50 explains the method of counting the granules at different levels. The volume of the granules was obtained by counting the number in a given volume and dividing by this number the weight of the substance




A—Illustrating Perrin's method of counting the number of atoms in a gram-molecule of a gas.

B—Counting the particles at different levels by determining the number visible in the flat field of a microscope objective adjusted at different heights.

FIG. 50.—Thinning out of the granules in an emulsion under the action of gravity.

contained in this volume of the suspension. Now this mean kinetic energy of one particle is equal to the kinetic energy of any single molecule at the same temperature and pressure. But we have seen (§ 43) that the pressure $p$ of a gas is given by

$$pv = \frac{1}{3} . nmu^2,$$

and since $\frac{1}{2}mu^2$ is the kinetic energy of a molecule we have

$$pv = \frac{2}{3} nw,$$

where $w$ is the kinetic energy of a molecule.

Now for a *gram-molecule* of gas,

$$pv = RT.$$

where $R$ is a constant. Considering a gram-molecule of a gas $n$ the number of molecules is $N$, the value we wish to find, and we obtain

$$\frac{2}{3}Nw = RT$$

or

$$w = \frac{3RT}{2N}.$$

Thus $w$, the mean kinetic energy, being found, and $R$ and $T$ being known, $N$ can be found. The values obtained by this method, and also by the kindred method of deducing the mean kinetic energy of a particle, from the average distance in any one direction travelled by the particle in a given time agree in giving the enormous value of about $69 \times 10^{22}$ molecules per gram-molecule (22·4 litres) of gas at N.T.P.

Another very accurate set of determinations of $N$ depend on the determination of the charge on one electron $e$. The charge on a gram molecule of ions each having a charge of one electron is $Ne$ and is equal to 96,494 coulombs (p. 132). We have then only to find $e$ to know $N$.

Millikan used the following ingenious and accurate method. Two metal plates, $P_1$, $P_2$, were separated by an air space and kept charged at a potential difference of some thousands of volts. A very fine spray of oil droplets was

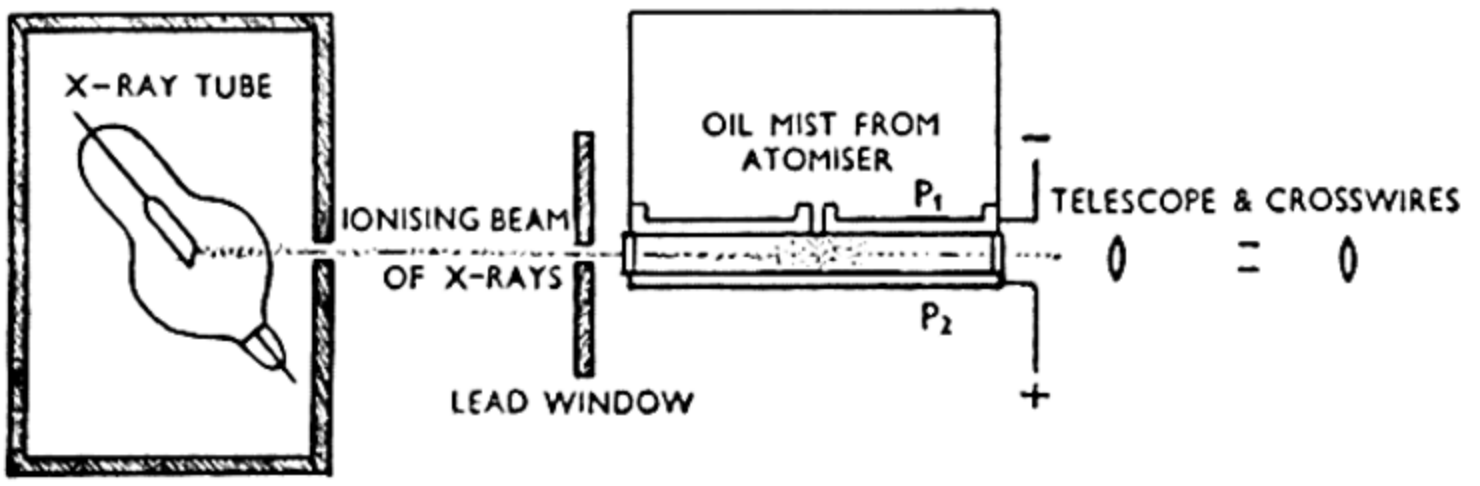



FIG. 51.—Diagram illustrating Millikan's method of determining the charge on an electron.

allowed to pass between them and the air was 'ionised' by means of X-rays setting free negative electrons and positively-charged ions. Now a droplet taking up a few ions or electrons became charged with a small multiple of $e$, the charge on one electron. This caused it to rise when positively charged and fall when negatively charged. The drop was illuminated by a beam of light and viewed by a telescope with cross-hairs, and the time necessary for it to rise or fall ·5222 cm. measured. A particular droplet was found to have a few sharply-fixed velocities depending on the number (1–9) of electrons settling on the oil drop, an intermediate value never being found. From these velocities and the P.D. between the plates $\frac{e}{m}$ was calculated, where $m$ is the mass of the oil-droplet. This was found from its rate of fall under gravity, using Stokes' law. The electronic charge was thus found to be $4{\cdot}774 \times 10^{-10}$ electrostatic units or $1{\cdot}592 \times 10^{-20}$ electromagnetic units. The charge on a gram-ion is 9649·4 electromagnetic units and the number of ions in a gram-ion is therefore

$$\frac{9649{\cdot}4}{1{\cdot}592} \times 10^{20}$$

$$= 6{\cdot}062 \times 10^{23}$$

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This will also be the number of molecules in a gram-molecule.

Recent work has shown that in applying Stokes' Law to the fall of the oil-droplet, Millikan employed a value for the viscosity of air which was incorrect. If the accepted value for the latter is inserted the electronic charge becomes $4{\cdot}816 \pm {\cdot}013 \times 10^{-10}$ electrostatic units, and the number of ions in a gram-ion $6{\cdot}02 \times 10^{23}$.

At least seven quite different ways of determining $N$ have been found, and they all give values within some 10 per cent. The most accurate and recent experiments indicate that the most probable figure for the number of molecules in a gram-molecule of a substance is $6{\cdot}021 \times 10^{23}$. The stupendous figure of $6{\cdot}02 \times 10^{23}$ molecules in 22·4 litres of gas cannot be grasped, and one can only hope to devise a few illustrations which may help to convey its magnitude. One of the tiny bubbles which collect on the sides of a glass of soda water contains as many molecules as there are sand grains in two hundred and fifty acres of sand, a yard in depth. Another striking illustration is given by Sidgwick: "If a tumblerful of water is poured into the sea, and in the course of time this becomes uniformly distributed through the sea, the rivers and all the other waters in or surrounding the earth; and if then a tumblerful of water is taken from any sea or river, this will contain about 1,000 of the molecules that were in the original tumbler."

In fact, the reader's cup of tea probably contains some thousand molecules of the water which Socrates drank in his hemlock draught.

**138. The Electron.**—The size, then, of the atoms and molecules and their numbers in a given quantity of matter are known with fair accuracy. The structure of the atom might well have seemed utterly beyond reach, and indeed until the last decade of the nineteenth century there was no evidence that the atom had any structure at all. The first step was the discovery by Crookes of a 'fourth state of matter' in the electrical discharges in a highly exhausted tube. These particles, streams of which constituted these discharges, weighed by a method in some respects analogous to that of the mass-spectrograph (p. 178), were found to have a mass of only 1/1840 of that of a hydrogen atom. These particles, which were called 'electrons,' were negatively charged and could be obtained from all kinds of matter by the influence of high temperatures, X-rays, etc. The electrons obtained from various kinds of matter were found to be identical and the electron was therefore considered to be a constituent of the atom. The atom is electrically neutral and so, since it contained these negatively-charged electrons, it evidently also contained positive electricity in some form. No free positive electron was definitely known to exist at this time.

Atoms from which negative electrons had been detached, were positively charged, but these were not thought to be ultimate particles.

**139. The Scattering of Alpha- and Beta-rays by Matter.**—Much light was thrown on the structure of the atom by the study of the effect of thin sheets of metal upon the $\alpha$-rays and $\beta$-rays of radio-active substances. These rays consist of a hail of material particles projected from radium and other radio-active elements at speeds varying from nearly that of light to about a hundredth of that value. The $\alpha$-rays are a stream of positively-charged helium atoms (the nuclei of helium, *i.e.*, helium atoms lacking the two negative electrons), and these particles have atomic weight 4; while the $\beta$-rays are a stream of negative electrons of weight only 1/1840 of that of a hydrogen atom.

When a beam of $\beta$-rays was allowed to traverse a piece of metal foil it was found to be scattered, clearly as a result of the repulsion of its particles by negatively-charged particles—electrons—contained in the atoms of the metal foil. From the degree of scattering it was found possible to calculate the number of electrons responsible for the scattering, and the number of these per atom of the metal constituting the foil was found to be about half the atomic weight of the atoms in question. Thus the gold atom (A.W. 197) appeared to contain about 100 electrons, the aluminium atom (A.W. 27) about 14. No information could be obtained as to the way in which these electrons were distributed in the atom, nor was any information available as to how the positive electricity in the atom was distributed. One fact was clear. The hundred electrons apparently contained in a gold atom had in all about a twentieth of the mass of a hydrogen atom, while the whole atom had two hundred times this mass. Clearly the mass of the atom was else where than in the negative electrons.

The next piece of evidence was derived from the bombardment of a piece of gold-leaf by $\alpha$-rays, whose course was measured by the effect of their ionised trails on a photographic plate. It was found that while almost all the $\alpha$-particles were but little deflected (average scattering 0·87°), a few, about one in twenty thousand, were turned through a large angle (*c.* 90°) or even deflected backwards. Now to deflect an $\alpha$-particle something near its own mass is needed. The negative electrons known to be in the atom had about one seven-thousandth of the mass of an $\alpha$-particle, and would deflect it about as much as a pea would deflect a cannon-ball. It thus became clear that there was something in the atom which was relatively and absolutely small, for only about one $\alpha$-particle in twenty thousand could hit it. Sir Ernest Rutherford, on these facts, built a theory of atomic structure which has since been modified but not materially altered.

**140. The Nucleus of the Atom.**—Rutherford concluded that the facts were accounted for by the assumption that the atom consists of a very small positively-charged nucleus, the mass of which is nearly equal to that of the atom and the charge of which is equal and opposite to the total charge of all the negative electrons outside it. Round this positive nucleus are distributed a cloud of negative electrons. On this theory the ultimate positive particle was identical with the ion of hydrogen and was given the name of ***proton***.

At this stage it was correctly concluded that :

(1) The atom had a small positively-charged nucleus of charge, $Ne$, where $N$ is the number of negative electrons outside the nucleus and $e$ the charge on one electron.

(2) $N$ was about one half the atomic weight.

Now one half the atomic weight is very roughly equal to the atomic number, *i.e.*, the ordinal number denoting the position of the element in the periodic table. In 1912 it was suggested that the number of electrons outside the nucleus might be equal to the atomic number ; one step onward in the periodic table corresponding to the addition of one unit of positive charge to the nucleus. The suggestion was not, however, adopted for some years.

**141. Radioactivity.**—This large subject can hardly be discussed in a few paragraphs, and Chapter XXVI. contains a treatment of radio-activity and the radio-active elements much more detailed than any which can be given here. It was found by Becquerel, in 1896, that certain elements gave out ' rays ' capable of affecting a photographic plate. Investigation of this phenomenon by the Curies, Rutherford, Soddy and others gradually elucidated a number of most remarkable facts, of which the following have a bearing on the structure of the atom.

(1) The elements which manifest this phenomenon have atomic weight greater than [1] 207 and all elements of greater atomic weight than bismuth (209) are radioactive.

(2) The ' rays ' given out are of three kinds—

(i.) $\alpha$-rays. These are a stream of *$\alpha$-particles* (which consist of the nuclei of helium atoms : A.W. 4) projected with an enormous velocity which varies with the element producing them, and is greater than a hundredth of the velocity of light (300,000 km./sec.).

(ii.) $\beta$-rays. These consist of a stream of negative electrons travelling with velocities little less than that of light.

(iii.) $\gamma$-rays. These do not consist of material particles, but are electro-magnetic vibrations of the character of light or X-rays, but of much shorter wave-length even than the latter.

(3) When an element emits $\alpha$- or $\beta$-rays it is transformed into another element. Since the removal of electrons from the outer rings of the atom does not produce a new atom but only an ion (§§ 115, 153), evidently the electrons and helium nuclei are formed from the nucleus of the atom.

(4) If an $\alpha$-particle is emitted, the new element formed in this way is the one which has *atomic number* less by two than the element from which it was formed ; *i.e.*, the new element formed is two places to the left of the old in the periodic table. Its *atomic weight* is diminished by *four* units. Thus an atom of radium (A.N. 88 ; A.W. 226) gives out an $\alpha$-particle (helium nucleus A.W. 4) and becomes emanation (A.N. 86 ; A.W. 222).

If a $\beta$-particle is given out then the atomic weight is unaltered, but the element increases its atomic number by one, moving one place in the periodic table to the right.

(5) It was found that two or more elements of different atomic weights and radio-active properties, and therefore with different nuclei, could occupy the same place in the periodic table. Such elements are called *isotopes* and have

[1] But see § 257.

chemical and physical properties so nearly alike as to be indistinguishable by chemical tests (§§ 148–151).

It appeared then from these facts that the place of an element in the periodic table did not depend on the atomic weight—the number of protons in the nucleus—but rather on the total *charge* on the nucleus (number of protons — number of electrons); for if an atom loses one $\alpha$-particle (charge 2 $\oplus$) and two $\beta$-particles (charge 2 $\ominus$) its place in the periodic table is unchanged though its atomic weight is diminished by four units. It seemed reasonable to suppose that the atomic number, denoting the place in the periodic table, is equal to the total positive charge on the nucleus, *i.e.*, to the difference between the number of positive electrons (A.W.) and negative electrons in the nucleus. The number of negative electrons in the outer rings must be equal to this number, for the whole atom is electrically neutral.

This theory had at a later stage to be slightly modified. In 1932 Chadwick discovered a particle which he called the *neutron*. The mass of this is equal to that of a proton but it has no charge.

Since the electron is larger than the nucleus there was difficulty in supposing that the nucleus contained a large number of electrons, and for this and other reasons it is thought that the nucleus consists of protons and neutrons only.

Thus if the atomic weight of an element is $W$ and its atomic number is $N$, we suppose its nucleus to contain $W - N$ neutrons and $N$ protons.

When a radioactive nucleus emits a $\beta$-particle (electron) it is supposed that 1 neutron changes into 1 proton, which remains in the nucleus, and 1 electron which is emitted.

**142. X-ray Spectra and Atomic Number.**—A remarkable piece of work which appeared in 1912 was performed by Moseley, who was, unfortunately, killed in the war of 1914–1918. He examined the X-ray spectra of various elements, spectra which had been inaccessible because at that date it was impossible to rule a grating fine enough to analyse these short waves. Moseley used a crystal of potassium ferrocyanide, the regular lines of atoms in which (§ 103) acted as an exceedingly fine grating.

He found that these spectra were of a simple type, and he established the fact that *the square root of the frequency of the rays which made up the highest frequency line in the X-ray spectra of an element was proportional to the atomic number of the element.* This gave us for the first time a means of finding the place of an element in the periodic table *by direct experiment* and so discovering how many elements were missing in the periodic table. Assuming hydrogen to be the lightest and uranium the heaviest, it appears that all the possible elements have now been discovered except those of atomic numbers 85 and 87.

At the time of the war of 1914–1918, by which scientific research was greatly hampered, we had, then, got a fairly clear idea of atomic structure. The atom was believed to have a very small nucleus containing both positive and negative particles, and round this was a crowd of electrons, probably rotating in rings, the arrangement of which was, it was thought, in some way related to the recurrent properties of atoms as shown in the periodic table.

**143. The Limitations of the Human Imagination in the Study of Atoms.**—The next and greatest advance was to discover how these electrons moved, if they moved at all, how they were arranged and how such arrangement influenced chemical and physical properties. This problem has been

partly solved. The work of Niels Bohr and others has now given a very fair idea of how the nucleus and surrounding electrons are related and has gone far to explain the mechanism of chemical combination. The work is far from being a complete and accurate representation of the atom and its electrons, but, nevertheless, it must contain a considerable substratum of truth. The most recent tendency is to ignore any mental picture of an atom we may form as being probably misleading and to rely simply upon the mathematical statements of the behaviour of the atom. To most of us, however, these are largely unintelligible, and it is best, at first, to visualise an "atomic model" which must be fairly close to the reality. Continuous effort is necessary to prevent ourselves thinking of an electron as a little object like a shot or a marble and to realise that it is not in the least like our everyday idea of matter, but probably a good deal more like an electromagnetic wave, itself a difficult enough thing to picture.

**144. Arrangement of Electrons Round the Nucleus.**—It seems reasonable to suppose that the electrons round the nucleus must either be stationary or moving. If they are stationary they should at once drop into the nucleus. Rutherford therefore supposed they were rotating round the nucleus and kept away from it by the centrifugal force engendered by their rotation. The difficulty then arises that an electrical charge rotating in this manner should, according to the accepted ideas of electro-dynamics, give rise to electromagnetic vibrations and so radiate energy. The energy so radiated would be gained at the expense of the electron's kinetic energy; its rotation would slow down and it would finally drop into the nucleus.

From this dilemma a means of escape was afforded by the *quantum theory*. It had been evident since about 1900 that ordinary dynamics was not applicable to radiation. In order to account for many facts concerned with radiation Planck put forward his theory of *quanta*. He supposed that energy of vibration could only be given out or taken up in *quanta*, small portions, the size of which is $h\nu$ where $h$ is a universal constant and $\nu$ is the frequency of the vibration of the system taking up energy. The quantum of energy is not like the electron, an absolutely fixed quantity, but varies with the frequency of the vibrating system producing the energy. The quantum theory has been so successful in accounting for numerous physical phenomena that it may be regarded as established.

In order to get over the difficulty that, according to 'classical' electrodynamics, the electrons, whether fixed or rotating, must fall into the nucleus, Bohr made certain assumptions, which went beyond Planck's quantum theory but which, by their results, seem to be justified.

**145. Bohr's Theory of Atomic Constitution.**—Bohr assumes: (1) When an electron rotates round the nucleus in any one orbit it emits no energy. The electron may have $n$ orbits corresponding to the possession by it of 1, 2, 3 . . . $n$ quanta of energy. The energy, E, of the electron is then given by $E = nh\nu$ where $n$ is an integer and $h$, $\nu$ have the meanings indicated above.

(2) An electron, he assumes, radiates energy *only* when passing discontinuously from one state or orbit to another of smaller energy. If its first energy was $E_1$ and the second $E_2$, the frequency $\nu$ of the emitted radiation is given by $E_1 - E_2 = h\nu$.

This theory was certainly plausible, but its real value appeared when it

was put to the test of accounting for the *kind* of radiation that atoms emit. It is well known that a glowing vapour or, in general, an atom in possession of much energy produces light which can be analysed spectroscopically into lines. That is to say, the radiation from atoms is of a small number of fixed frequencies, each corresponding to a spectroscopic line. If radiation was emitted by the rotating electron, on the classical theory all frequencies should be represented in the spectrum. One of the chief triumphs of Bohr's theory was in the calculation from his assumptions, coupled with those of the theory

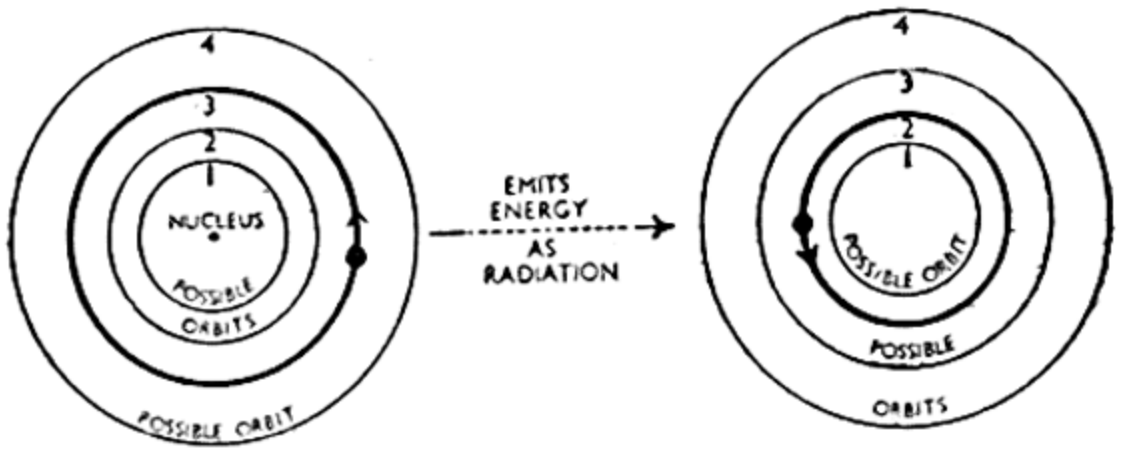



FIG. 52.—Bohr's theory: Radiation is emitted by an atom as the result of an electron passing from its orbit to another orbit of smaller energy.

of relativity, of the positions of all the lines in the hydrogen spectrum, a feat so remarkable that twenty years ago we might have expected to wait a century for its performance.

The spectral lines of ionised helium have also been calculated and found to correspond in every detail with the known spectra. The details of the spectra of more complicated atoms have not yet been calculated. but the results already attained are highly convincing. Moreover, the deduction of the atomic structures of more complex elements from their spectra and the confirmation of the truth of these deductions by chemical evidence affords an almost equally convincing evidence that Bohr's theory corresponds in many respects with the facts.

None the less Bohr's views led to wrong results in some details, and the modern view of the atom differs a good deal from Bohr's, chiefly in the discarding of his assumption that the electrons are revolving in orbits.

Let us, before proceeding further, summarise the present state of knowledge as to the constitution of the atom.

(1) Atoms are composed of neutral particles (neutrons) and positive units of electricity (protons) and negative units of electricity (electrons) with an equal and opposite charge.

(2) The protons and neutrons [1] constitute a *nucleus* small in size compared with the whole atom. The electrons are distributed in well-defined groups round this nucleus.

If $N$ is the atomic number of the element and $W$ its atomic weight the nucleus contains $N$ protons [2] and $W - N$ neutrons (total charge $+ Ne$). The outer electrons are $N$ in number (total charge $- Ne$).

Thus sodium has atomic number 11, atomic weight 23. There are, therefore, 11 protons and 12 neutrons in the nucleus of a sodium atom and 11 electrons in the surrounding groups.

(3) Bohr pictured the electrons as taking up orbits corresponding to the possession of from one to six quanta of energy. We prefer to regard

[1] Except in the case of hydrogen.
[2] For the case where $W$ is not a whole number, *v.* § 149.

the electrons as forming concentric groups or shells whose diameter corresponds with the number of quanta, without specifying anything about their motion. It is sufficient to realise that if an atom contains electrons with say 1, 2 and 3 quanta respectively, the 3-quanta electrons will be the outermost and the 1-quantum electrons the innermost.

We will now consider what will be the configuration of the lighter atoms in their state of least energy with all the electrons in their lowest orbits.

**146. Structure of the Individual Atoms.**—*First period of the periodic table.* Hydrogen has one 1-quantum electron and its nucleus is a single proton. This arrangement is deducible from its spectrum.

The second element, helium, has atomic weight 4, atomic number 2. Thus it has a nucleus of 2 protons and 2 neutrons and has 2 electrons both in the 1-quantum group. This inner pair of electrons in 1-quantum group is found in all elements, and their loss or gain of quanta give rise to the X-ray spectra (p. 167).

*Second Period.*—The element lithium, which follows helium, has atomic number 3 and atomic weight 7. It has, therefore, 3 protons and 4 neutrons in the nucleus and 3 electrons in the outer groups. An arrangement of three 1-quantum electrons is evidently unstable and the third enters the 2-quantum group.

Now this third electron is much more easily removed than the two electrons of the helium atom, for it lies further from the sphere of attraction of the nucleus. We shall find throughout that the structure of an inert gas always represents a peculiarly stable system of electrons. This is the reason for their inertness, for chemical combination involves an interference with the outer electrons resulting in a more stable state. As we pass along the second period each element has an atomic number one greater than the last and, therefore, one more electron in the outermost group of electrons. Thus we have for each of the elements of the second period :—

(1) Nucleus.
(2) Two electrons in the 1-quantum group surrounded by
(3) From 1–8 electrons in the 2-quantum group.

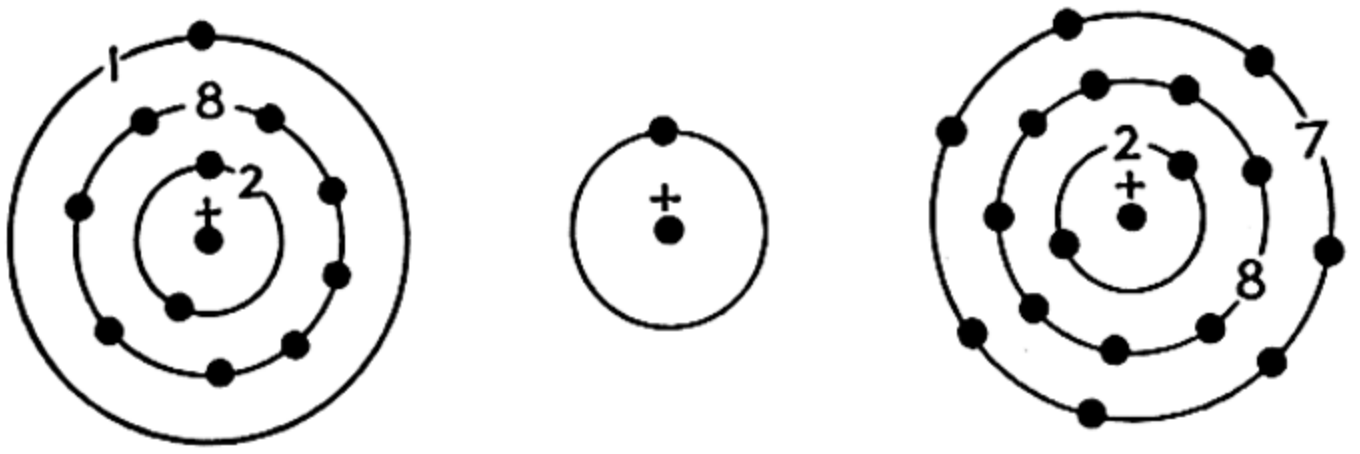
*Elements of First and Second Periods.*

| Period. | Atomic Number. | Symbol. | Electrons in One-quantum group. | Electrons in Two-quanta group. |
|---|---|---|---|---|
| | | | 1 | 2 |
| 1 | 1 | H | 1 | — |
| | 2 | He | 2 | — |
| | 3 | Li | 2 | 1 |
| | 4 | Be | 2 | 2 |
| | 5 | B | 2 | 3 |
| | 6 | C | 2 | 4 |
| | 7 | N | 2 | 5 |
| | 8 | O | 2 | 6 |
| | 9 | F | 2 | 7 |
| | 10 | Ne | 2 | 8 |

With neon we reach the maximum number of 2-quanta electrons and with it a peculiarly stable arrangement. The next electron added goes into the 3-quantum group and the element—sodium—so produced is the analogue of lithium, which has a similar solitary electron in the 2-quantum group.

*Third Period.*—The next period, sodium—argon, reproduces the last in general structure. Each element has in successive (though interpenetrating) layers:

(1) Nucleus.
(2) Two electrons in the 1-quantum group.
(3) Eight electrons in the 2-quantum group.
(4) From 1–8 electrons in the 3-quantum group.




Sodium atom. Hydrogen atom. Chlorine atom.

FIG. 54.

Thus the sulphur atom, for example, has the structure,

| Electrons in | 1-quantum group | 2-quantum group | 3-quantum group |
|---|---|---|---|
| | 2 | 8 | 6 |

and we end the period with an inert gas, argon, with the structure:

| Electrons in | 1-quantum group | 2-quantum group | 3-quantum group |
|---|---|---|---|
| | 2 | 8 | 8 |

The complete layer of eight electrons again shows its peculiar stability and the fourth period here begins.

*Fourth Period.*

| Atomic Number. | Symbol. | | Electrons in groups having | | | |
|---|---|---|---|---|---|---|
| | | | 1 quantum. | 2 quanta. | 3 quanta. | 4 quanta. |
| 19 | K | | 2 | 8 | 8 | 1 |
| 20 | Ca | | 2 | 8 | 8 | 2 |
| 21 | Sc | TRANSITION ELEMENTS | 2 | 8 | 9 | 2 |
| 22 | Ti | | 2 | 8 | 10 | 2 |
| 23 | V | | 2 | 8 | 11 | 2 |
| 24 | Cr | | 2 | 8 | 13 | 1 |
| 25 | Mn | | 2 | 8 | 13 | 2 |
| 26 | Fe | | 2 | 8 | 14 | 2 |
| 27 | Co | | 2 | 8 | 15 | 2 |
| 28 | Ni | | 2 | 8 | 16 | 2 |
| 29 | Cu | | 2 | 8 | 18 | 1 |
| 30 | Zn | | 2 | 8 | 18 | 2 |
| 31 | Ga | | 2 | 8 | 18 | 3 |
| 32 | Ge | | 2 | 8 | 18 | 4 |
| 33 | As | | 2 | 8 | 18 | 5 |
| 34 | Se | | 2 | 8 | 18 | 6 |
| 35 | Br | | 2 | 8 | 18 | 7 |
| 36 | Kr | | 2 | 8 | 18 | 8 |

*Fourth Period.*—The first element, potassium, has one more electron than argon, but although an atom can contain up to 18 3-quantum electrons, and only eight are present, this goes into the 4-quantum group. So also calcium, the second element, has two 4-quantum electrons in a manner exactly analogous to beryllium and magnesium. But the third element, scandium, does not have three 4-quantum electrons. It retains the two 4-quantum electrons of calcium, but the new electron goes into the 3-quantum group. This behaviour is characteristic of the transition elements (pp. 156–157). All of these have one or two electrons only in their outermost groups, while each successive element has one more 3-quantum than the last. This process continues until all the possible places for 3-quantum electrons are filled.

Consequently we find a series (21–28) of ' transition elements ' with variable valency, coloured ions and other characteristic properties. As soon as the full eighteen possible electrons have gone into the 3-quantum group the succeeding elements have each one more 4-quantum electron than the last and so a series of elements (Ga-Kr) exactly analogous to those of the short periods follows.

*Fifth Period.*—This is quite analogous to the fourth.

*Sixth Period.*—In this a new phenomenon appears. At the beginning of this period we start with an alkali metal, cæsium, with a single outermost 6-quantum electron, while both the 5-quantum group and the 4-quantum group are not yet filled up. When after two elements (as in the fourth period) the 5-quantum group (the next layer to the outermost) begins to be filled in we get transition elements formed (La), but while the 4-quantum group, two layers deep in the atom, are being filled in we get the series of rare earths —elements remarkably alike because their only structural differences are in the inner parts of the atom shielded by two electron layers (§§ 506–508).

**147. The Groups and their Structure.**—It may be instructive to compare the structure of members of the same group but different periods. We may first consider the group of inert gases (Group 0).

| Inert Gas. | Electrons in Groups having | | | | | |
|---|---|---|---|---|---|---|
| | 1 quantum. | 2 quanta. | 3 quanta. | 4 quanta. | 5 quanta. | 6 quanta. |
| Helium . | 2 | | | | | |
| Neon . . | 2 | 8 | | | | |
| Argon . | 2 | 8 | 8 | | | |
| Krypton . | 2 | 8 | 18 | 8 | | |
| Xenon . | 2 | 8 | 18 | 18 | 8 | |
| Emanation . | 2 | 8 | 18 | 32 | 18 | 8 |

The typical feature of an inert gas is then an atom having a completed outer layer to which no more electrons can be added. This is evidently a highly stable type of atom.

As a second illustration we may take the alkaline-earth metals (Group II. A).

These alkaline-earth elements, then, are characterised by the possession of an outer incomplete layer of two electrons, all the inner rings being complete.

| | Electrons in Groups having | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 quantum. | 2 quanta. | 3 quanta. | 4 quanta. | 5 quanta. | 6 quanta. | 7 quanta. |
| Beryllium | 2 | 2 | | | | | |
| Magnesium | 2 | 8 | 2 | | | | |
| Calcium . | 2 | 8 | 8 | 2 | | | |
| Strontium. | 2 | 8 | 18 | 8 | 2 | | |
| Barium . | 2 | 8 | 18 | 18 | 8 | 2 | |
| Radium . | 2 | 8 | 18 | 32 | 18 | 8 | 2 |

These outer electrons can be detached, forming ions such as $Ba^{++}$, and consequently the elements are divalent.

Finally, we may take a set of transition elements, say Group VI. A.

| | Electrons in Groups having | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 quantum. | 2 quanta. | 3 quanta. | 4 quanta. | 5 quanta. | 6 quanta. | 7 quanta. |
| Chromium . | 2 | 8 | 13 | 1 | | | |
| Molybdenum | 2 | 8 | 18 | 13 | 1 | | |
| Tungsten . | 2 | 8 | 18 | 32 | 12 | 2 | |
| Uranium . | 2 | 8 | 18 | 32 | 18 | 13 | 1 |

Each of these elements has the outer two groups, consisting of 13 and 1 (or 12 and 2) electrons, respectively. This group of 13 electrons contains a sub-group of eight which cannot be detached, while the remainder can. These latter electrons and the single outer electron are readily detached, so that six electrons (or a less number) can be removed for chemical combination and we find in chromium, for example, valencies of 2, 3 and 6.

The structure of the atom then provides a clear explanation of the remarkable regularities of the periodic table, and still more convincingly explains many of the peculiar irregularities which had always been noticed and had even been regarded as a fatal defect in the table, considered as an expression of the relationships of the chemical elements. The above system is not to be regarded as the last word on the subject of atomic structure. None the ess, it remains the practical working theory of chemists, and is at least a very close approximation to the truth.

**148. Isotopes.**—The term *isotope* was invented by Soddy in 1913 to denote elements which, though having different atomic weights, had identical chemical properties, and consequently occupied the same place in the periodic table. These radio-active isotopes are discussed in some detail in Chapter XXVI. The case of outstanding interest was that of lead. It was shown that in radio-active changes uranium (238) lost eight $\alpha$-particles (atomic weight 4) and changed into lead, which should, therefore, have atomic mass $238 - 8 \times 4 =$

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206, while thorium (atomic weight 232) lost six $\alpha$-particles and also became lead, should which have atomic weight $232 - 6 \times 4 = 208$. Soddy predicted that a difference in atomic weight would be found in lead from thorium and uranium minerals respectively. This was found to be the case (§ 630), and these two kinds of lead were found to differ in atomic weight by about two units, but were indistinguishable in all properties which did not depend on atomic weight.

The atomic theory of Dalton (§ 36) stated that atoms of the same kind all had the same mass. This was not a justifiable assumption. All the chemical laws would be just as well explained if the atoms of any one element had always, in any considerable portion, the same *average* mass. The weighing of individual atoms has not been attempted until recently, and all 'atomic weights' were averages based on the weighing of such a great number of atoms (more than $10^{20}$), that all individual differences would be smoothed out. Thus the weight of a man is a highly variable quantity, say 8–18 stone, a divergence of up to 50 per cent. of the mean being common, but the weight of a thousand men taken at random will vary very much less in proportion, a difference of 1 per cent. between two successive thousands being very unlikely.

The method of positive ray analysis of Sir J. J. Thomson gave a rough method of estimating the weights of individual atoms. In this method, which cannot be here described in detail, a beam of rapidly-moving positively-charged atoms is subjected to an electromagnetic field, which causes the individual atoms to travel in courses, the locus of which is a parabola of size and shape depending on the mass of the atoms concerned. These parabolas were received on a photographic plate. The method at first indicated that all atoms of the same kind had the same mass, but the element neon was found to give a distinct double trace indicating atoms of two different masses. Aston, in 1919, devised the mass-spectrograph which he has since improved so as to measure the individual atomic weights with an error of less than 1 in 10,000.

Figs. 55 and 56 give a rough idea of the construction of a mass-spectrograph. An X-ray bulb, B, has an anode, A, of aluminium, and a perforated cathode, C, of the same metal. A silica bulb, D, receives the concentrated stream of electrons from the cathode. A minute leak allows the entry of a trace of the vapour of some volatile compound of the element, the atomic weights of the atoms of which are to be determined. Atoms (or molecules) of the element become positively charged as a result of the detachment of electrons. These ions are attracted to the negatively-charged cathode and a few pass through the perforation in the cathode, forming a beam of rapidly-moving and positively-charged atoms or molecules. From these rays of charged atoms, travelling with varying velocities, a thin ribbon is selected by the slits $S_1$ $S_2$. The atoms composing this ribbon are deflected by a powerful

electrostatic field to an extent given by $\frac{e}{mv^2}$, *i.e.*, directly as their charge and inversely as their kinetic energy. A group of these rays is selected by the diaphragm (Fig. 55), and then passes between the poles of a powerful electromagnet of which the field is so arranged as to bend the rays in the opposite direction. It can be shown that this deflection is proportional to $\frac{e}{mv}$, and by suitably adjusting the strength of the fields it is possible to deflect the rays

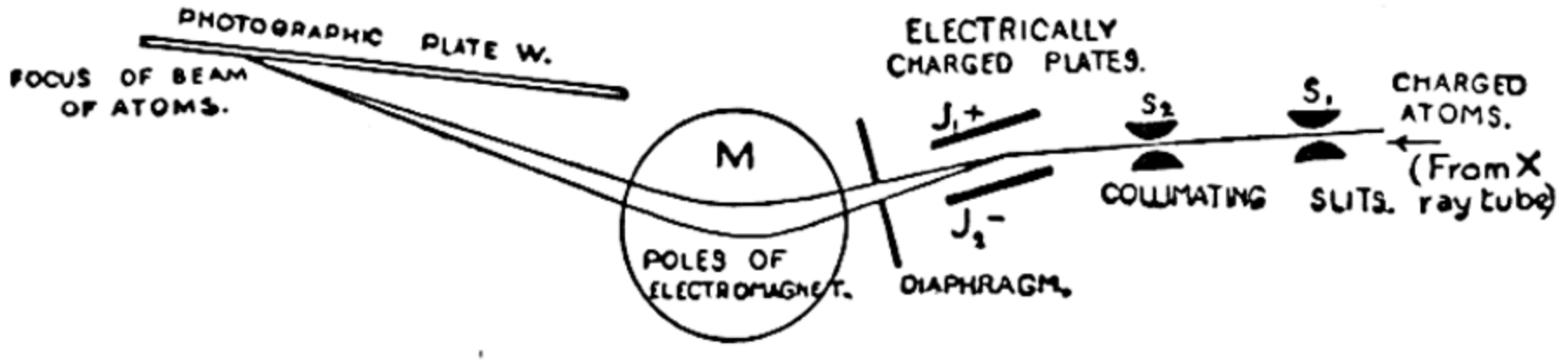



FIG. 55.—Aston's Mass-spectrograph.

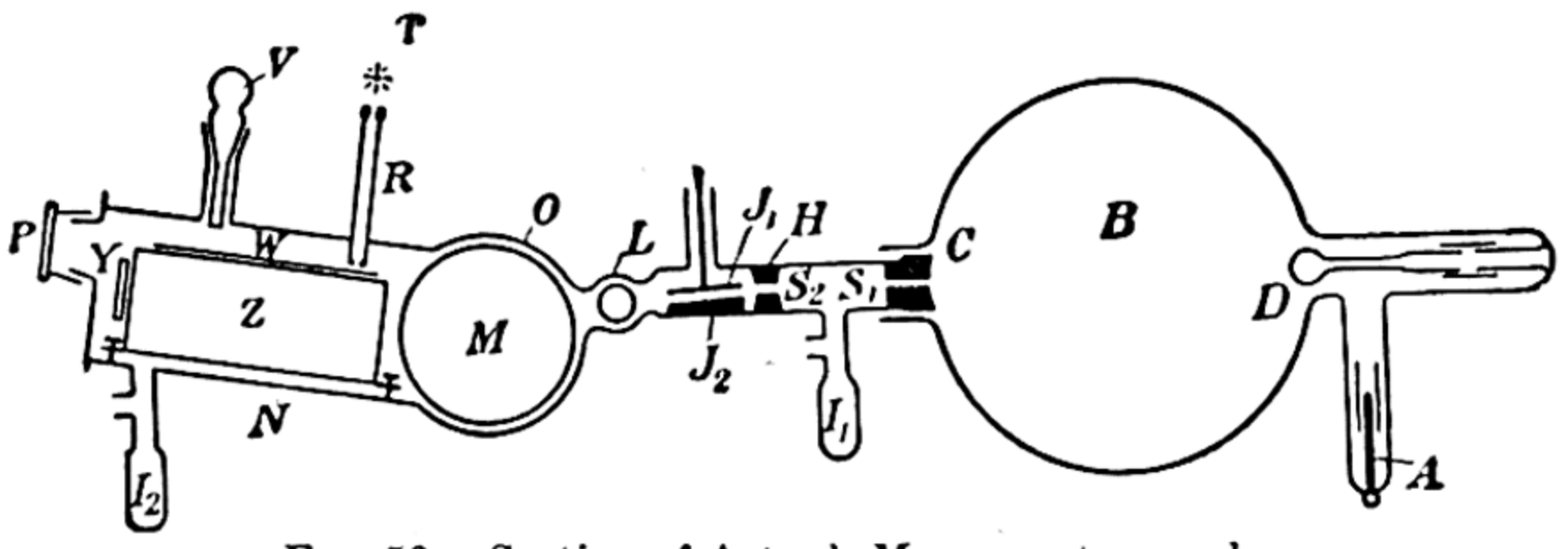



FIG. 56.—Section of Aston's Mass-spectrograph.

in such a way as to bring them to a focus, the position of which depends on $m$ only. A photographic plate receives the flying ions at their focus and is thus marked with a series of lines each corresponding to a group of atoms of the same mass. Some common atoms, which are always present, give markings which can be recognised, and by measurement of the position of the lines relative to these markings the mass of the particles causing them can be deduced.

Several improvements and modifications in the apparatus have been made, but the above gives a sufficiently close approximation to the method as now carried out.

As a result of these investigations almost all of the elements have been shown to be complex in character, as is shown in the table appended (pp. 180–182).

**149. Prout's Hypothesis.**—It has been noticed at an early date that atomic weights were much more often nearly whole numbers than would be expected if they were merely a set of numbers taken at random. Prout, in 1815, suggested that the atoms of all elements were made up of smaller atoms of some primordial substance. He suggested that these were atoms of hydrogen. If this were true and if hydrogen were taken as the unit of atomic weight all atomic weights should be whole numbers. This was seen to be untrue, for chlorine, copper and several others were obvious exceptions.

When Rutherford put forward the theory (§ 140) that atoms were made up of protons (atomic weight 1·008) and electrons (atomic weight, c. 0·0005) it appeared that all elements should have atomic weights within a small fraction of a whole number for all atomic weights would be (1·008 + 0·0005) $n$. where $n$ is the number of protons present. It soon appeared that another factor influenced this result and it seemed likely that energy had been liberated in great quantities when protons combined, at some time in the remote past, to form a nucleus, and this energy, according to the relativity theories, was equivalent to a certain mass.

Thus, for example, the helium atom contains:

| | | |
|---|---|---|
| 2 protons and 2 neutrons . . . . . | Mass. . | 4·032 |
| 2 electrons . . . . . | Mass c. . | 0·002 |
| | | 4·034 |
| The actual atomic weight of helium is, however . . . . | | 4·003 |
| The difference being accounted for by the energy of formation of the helium nucleus equal to 700,000 cals. per gm.-atom of helium, equivalent to a mass of . . . . . | | 0·031 |
| | | 4·034 |

These considerations, however, made it more, rather than less, probable that atomic weights should be, at any rate, nearly whole numbers.

The explanation of fractions of a unit occurring in atomic weights was found, as a result of the use of the mass-spectrograph, to be the fact that many elements were mixtures of two or more *isotopes*, identical in chemical properties and in such physical properties as do not depend on atomic weight. Thus, neon, of atomic weight 20·2, was shown to be a mixture of two neons, one of atomic mass 20 and the other of atomic mass 22. Chlorine, of atomic weight 35·46, was also found to consist of two kinds of atoms of atomic mass 35 and 37.

The examination of the remaining elements showed that their atoms all had masses which were nearly whole numbers if the weight of an oxygen atom be called 16·000. The divergence from whole numbers due to the "packing" effect resulting from the liberation of energy in their formation amounts at most to about 0·09 units.

The table given below is that issued by the Chemical Society for 1929 modified to include more recent work.

## ATOMIC WEIGHTS AND ISOTOPES. 1949.

| Atomic number. | Name. | Symbol. | Atomic Weight. | Mass-numbers of Isotopes in Order of Intensity. |
|---|---|---|---|---|
| 1 | Hydrogen . | H | 1·0080 | 1, 2 |
| 2 | Helium . | He | 4·003 | 4 |
| 3 | Lithium . | Li | 6·940 | 7, 6 |
| 4 | Beryllium . | Be | 9·02 | 9 |
| 5 | Boron . . | B | 10·82 | 11, 10 |
| 6 | Carbon . . | C | 12·01 | 12, 13 |
| 7 | Nitrogen . | N | 14·008 | 14, 15 |
| 8 | Oxygen . | O | 16·0000 | 16, 18, 17 |

| *Atomic number.* | *Name.* | *Symbol.* | *Atomic Weight.* | *Mass-numbers of Isotopes in Order of Intensity.* |
|---|---|---|---|---|
| 9 | Fluorine . | F | 19·00 | 19 |
| 10 | Neon . . | Ne | 20·183 | 20, 22, 21 |
| 11 | Sodium . . | Na | 22·997 | 23 |
| 12 | Magnesium . | Mg | 24·32 | 24, 25, 26 |
| 13 | Aluminium . | Al | $26·97_0$ | 27 |
| 14 | Silicon . . | Si | 28·06 | 28, 29, 30 |
| 15 | Phosphorus . | P | 30·98 | 31 |
| 16 | Sulphur . | S | 32·06 | 32, 34, 33 |
| 17 | Chlorine . | Cl | 35·457 | 35, 37 |
| 18 | Argon . . | A | 39·944 | 40, 36, 38 |
| 19 | Potassium . | K | 39·096 | 39, 41, 40 |
| 20 | Calcium. . | Ca | 40·08 | 40, 44, 42, 43 |
| 21 | Scandium . | Sc | 45·0 | 45 |
| 22 | Titanium . | Ti | 47·90 | 48, 46, 47, 50, 49 |
| 23 | Vanadium . | V | 50·95 | 51 |
| 24 | Chromium . | Cr | 52·01 | 52, 53, 50, 54 |
| 25 | Manganese . | Mn | 54·93 | 55 |
| 26 | Iron . . | Fe | 55·85 | 56, 54, 57, 58 |
| 27 | Cobalt . . | Co | 58·94 | 59 |
| 28 | Nickel . . | Ni | 58·69 | 58, 60, 62, 61, 64 |
| 29 | Copper . . | Cu | 63·57 | 63, 65 |
| 30 | Zinc . . | Zn | 65·38 | 64, 66, 68, 67, 70 |
| 31 | Gallium . | Ga | 69·72 | 69, 71 |
| 32 | Germanium . | Ge | 72·60 | 74, 72, 70, 73, 76 |
| 33 | Arsenic . . | As | 74·91 | 75 |
| 34 | Selenium . | Se | 78·96 | 80, 78, 76, 82, 77, 74 |
| 35 | Bromine . | Br | 79·916 | 79, 81 |
| 36 | Krypton . | Kr | 83·7 | 84, 86, 82, 83, 80, 78 |
| 37 | Rubidium . | Rb | 85·48 | 85, 87 |
| 38 | Strontium . | Sr | 87·63 | 88, 86, 87 |
| 39 | Yttrium . | Yt | 88·92 | 89 |
| 40 | Zirconium . | Zr | 91·22 | 90, 92, 94, 91, 96 |
| 41 | Niobium . | Nb | 92·91 | 93 |
| | (Columbium) . | (Cb) | | |
| 42 | Molybdenum . | Mo | 95·95 | 98, 96, 95, 92, 94, 100, 97 |
| 43 | Technetium . | Tc | 99·0 | 96, 99 |
| 44 | Ruthenium . | Ru | 101·7 | 102, 101, 104, 100, 99, 96 |
| 45 | Rhodium . | Rh | 102·91 | 103 |
| 46 | Palladium . | Pd | 106·7 | 104, 105, 106, 108, 110, 102 |
| 47 | Silver . . | Ag | 107·880 | 107, 109 |
| 48 | Cadmium . | Cd | 112·41 | 114, 112, 110, 111, 113, 116, 106, 108 |
| 49 | Indium . . | In | 114·76 | 115 |
| 50 | Tin . . | Sn | 118·70 | 120, 118, 116, 119, 117, 124, 122, 112, 114, 115 |
| 51 | Antimony . | Sb | 121·76 | 121, 123 |
| 52 | Tellurium . | Te | 127·61 | 130, 128, 126, 125, 124, 122, 123 |
| 53 | Iodine . . | I | 126·92 | 127 |
| 54 | Xenon . . | Xe | 131·3 | 129, 132, 131, 134, 136, 130, 128, 124, 126 |
| 55 | Cæsium . | Cs | 132·91 | 133 |
| 56 | Barium . | Ba | 137·36 | 138, 137, 136, 135 |
| 57 | Lanthanum . | La | 138·92 | 139 |
| 58 | Cerium . . | Ce | 140·13 | 140, 142 |
| 59 | Praseodymium | Pr | 140·92 | 141 |

| *Atomic number.* | *Name.* | *Symbol.* | *Atomic Weight.* | *Mass-numbers of Isotopes in Order of Intensity.* |
|---|---|---|---|---|
| 60 | Neodymium . | Nd | 144·27 | 142, 144, 146, 143, 145 |
| 61 | Promethium . | Pm | 147·0 | 147 |
| 62 | Samarium . | Sm | 150·43 | 152, 154, 147, 149, 148, 150, 144 |
| 63 | Europium . | Eu | 152·0 | 151, 153 |
| 64 | Gadolinium . | Gd | 156·9 | 156, 158, 155, 157, 160 |
| 65 | Terbium . | Tb | 159·2 | 159 |
| 66 | Dysprosium . | Dy | 162·46 | 164, 162, 163, 161 |
| 67 | Holmium . | Ho | 164·94 | 165 |
| 68 | Erbium . | Er | 167·2 | 166, 168, 167, 170 |
| 69 | Thulium . | Tm | 169·4 | 169 |
| 70 | Ytterbium . | Yb | 173·04 | 174, 172, 173, 176, 171 |
| 71 | Lutecium . | Lu | 174·99 | 175 |
| 72 | Hafnium . | Hf | 178·6 | (176), 177, 178, 179, 180 |
| 73 | Tantalum . | Ta | 180·88 | 181 |
| 74 | Tungsten . | W | 183·92 | 184, 186, 182, 183 |
| 75 | Rhenium . | Re | 186·31 | 187, 185 |
| 76 | Osmium . | Os | 190·2 | 792, 190, 189, 188, 186, 187 |
| 77 | Iridium . | Ir | 193·1 | 193, 191 |
| 78 | Platinum . | Pt | 195·23 | 195, 196, 194, 198, 192 |
| 79 | Gold . . | Au | 197·28 | 197 |
| 80 | Mercury . | Hg | 200·61 | 202, 200, 199, 201, 198, 204, 196, 197, 203 |
| 81 | Thallium . | Tl | 204·39 | 205, 203 |
| 82 | Lead . . | Pb | 207·21 | 208, 206, 207, 204, 203, 205, 209, 210 |
| 83 | Bismuth . | Bi | 209·00 | 209 |
| 84 | Polonium . | Po | 210 | |
| 85 | Astatine | At | — | 211, 218 |
| 86 | Radon . . | Rn | 222 | |
| 87 | Francium | Fr | 223·0 | 223 |
| 88 | Radium. . | Ra | 226·05 | |
| 89 | Actinium . | Ac | — | |
| 90 | Thorium . | Th | 232·12 | 232 |
| 91 | Protoactinium | Pa | — | |
| 92 | Uranium . | U | 238·07 | 238, 235, 234 |
| 93 | Neptunium . | Np | 237 | 237, 238, 239 |
| 94 | Plutonium . | Pt Pu | 239 | 238, 239, 240, 241 |
| 95 | Americium | Am | 241 | 241, 242 |
| 96 | Curium | Cm | 242 | 240, 242 |

Considering the fact that so many elements consist of mixtures of two kinds of atoms it is very remarkable that their atomic weights, as determined by chemical methods, are in practice so constant. The only element of which the atomic weight varies according to its source is lead, which we know to be derived from at least two different sources, thorium and uranium. It seems likely that when the atoms were originally formed the isotopes were produced in certain fixed proportions and have never become separated.

**150. Separation of Isotopes.**—This is an exceedingly difficult problem, as the only differences between them are small differences of atomic weight. Quite a number of methods have, however, attained some success.

(a) A *mass spectrograph* has been designed to collect the atoms of different atomic weight on metal plates. Since the vapour in a mass spectro-

graph is at very low pressure only a few thousandths of a milligram can be collected : the separation is however complete.

(b) Since the gaseous isotopes differ in density it is possible to separate them by *diffusion*. The pure neon isotope $^{22}Ne$ has been separated by an apparatus in which ordinary neon underwent 50 successive diffusions.

(c) The method of *thermal diffusion* has recently proved a very effective one for the separation of gaseous isotopes. The apparatus consists simply of a hot vertical surface opposite to a cold one, *e.g.*, a hot wire stretched along the axis of a cold vertical glass tube. As a result of processes which have not been entirely elucidated, the heavier component of the gas-mixture becomes concentrated at the bottom of the tube, and repeated diffusions effect a considerable degree of separation.

(d) The *electrolysis* of a mixture of isotopes may give a product containing more of one than the other (see § 193 on the hydrogen isotope, deuterium). Lithium has been partly separated into $^{6}Li$ and $^{7}Li$ in this way.

(e) *Fractional Distillation* may have some success, *e.g.*, in partially separating ' heavy water ' from ordinary water.

The isotope of hydrogen of mass 2 is of such importance and differs so widely from the isotope of mass 1 that it has been thought best to treat it separately in § 193a.

**151. Atomic Structures of Isotopes.**—The explanation of the existence of isotopes follows readily from the modern theory of the structure of the atom. The atom consists of :—

(1) A nucleus, containing $N$ protons and $W-N$ neutrons, where $W$ is the atomic weight and $N$ the atomic number. The net positive charge of the nucleus is $+ N$. The mass of the nucleus determines the atomic mass.

(2) A set of electrons distributed round this nucleus. There are $N$ of these making a total negative charge $- N$, equal and opposite to that of the nucleus. On the number of these electrons depends the chemical and most of the physical properties.

Isotopes differ in the properties to be ascribed to the nucleus, *e.g.*, in atomic mass, and the properties derived from it such as density ; also in radioactivity, which is a nuclear property.

They are identical in the other properties which we have reason to assign to the outer electrons. We may assume, then, with reason, that isotopes have identical electronic groupings and consequently identical nuclear charge. They have, on the contrary, different nuclear masses. Now the nuclear charge $N$, is that of $N$ protons, and clearly the number of neutrons present will not affect this charge but will affect the atomic weight. Thus the two isotopes of neon may be represented diagrammatically thus :

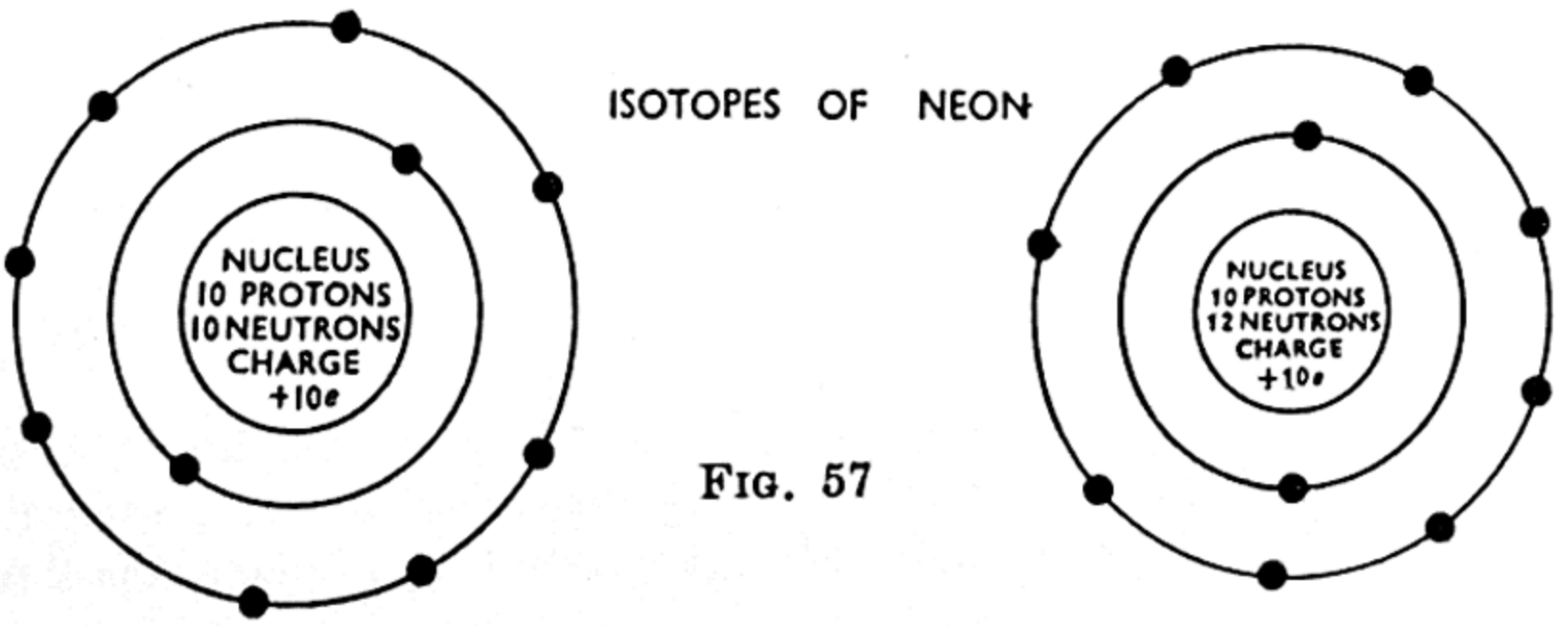



FIG. 57

The nuclei differ in composition and therefore in mass, but have the same charge (+ 10*e*). The electrons outside the nucleus are identical in each case.

**151a. Atomic Transmutation.**—When matter is bombarded with heavy particles travelling at enormous speeds, some of the nuclei of the atoms are struck, and of these some are disintegrated.

The electron (A.W. 0·0005) is not a heavy enough particle, but the $\alpha$-particle (helium nucleus, A.W. 4), the proton (A.W. 1), the deuteron (deuterium nucleus, A.W. 2), the neutron (§ 151b, A.W. 1) have all been used. The great speed in the case of the $\alpha$-particle and the neutron is inherent in the way they are formed. Protons and deuterons have to be accelerated by a powerful electric field.

The tracks of these particles can be photographed by the methods described in § 1260, and by studying the nature of the trails and the angles of deflexion of the products, inferences can be drawn as to the products. In most cases only a few atoms are broken up, and the extent of such transmutation is far beyond estimation by chemical means.

The general rule is that the nucleus of the atom bombarded takes up the bombarding particle, and then, becoming unstable, breaks up into two nuclei, which, of course, ultimately collect their complement of electrons.

The following transmutations are examples of this. The superscript figures are atomic weights :—

$$Li^{7} + H^{1} = 2He^{4}$$

Lithium + proton = two helium atoms.

$$B^{11} + H^{1} = 3He^{4}$$

Isotope of boron + proton = three helium atoms

$$B^{10} + He^{4} = H^{1} + C^{13}$$

Boron + $\alpha$-particle = hydrogen + isotope of carbon

A great number of transmutations have been described.

It may happen that nuclei which have taken up $\alpha$-particles do not break up immediately, but only in the course of minutes or hours. In this case the elements are said to be made artificially radio-active, a condition further described in § 1271–2.

**151b. The Neutron.**—Chadwick, in 1932, discovered that when beryllium is bombarded with $\alpha$-particles, particles of very long range are emitted. They are not deflected by an electric field, and consequently have no charge. Their mass is nearly that of a proton. It is concluded that the *neutron*, as this particle is termed, is a simple elementary constituent of matter like the proton and electron.

**151c. The Positive Electron.**—The positive electron or *positron* of charge + 1 and probably of the same mass as a negative electron, was discovered independently by C. D. Anderson and by P. M. S. Blackett and G. P. S. Occhialini.

It seems unlikely that it is a constituent of matter. It seems to be produced by the absorption by matter of radiation of very short wave-length [*e.g.*, certain $\gamma$-rays (§ 1255) ]. Little is as yet known about its relation to matter.

There is no certainty that we have exhausted all the possibilities of ultimate particles. The *neutrino*, *mesotron*, and *heavy electron* have been described, but as they are not normal constituents of matter they do not concern the chemist.

It seems that the only permanent and stable constituents of matter are the proton, the electron, and the neutron.

| | | | |
|---|---|---|---|
| I. | Electrons . . | Mass 1/1840 | Charge $-e$ |
| II. | Protons . . | Mass 1·008 | Charge $+e$ |
| III. | Neutrons . . | Mass 1·010 | Charge 0 |

## CHEMICAL COMBINATION, VALENCY, AND THE STRUCTURE OF THE ATOM

**152. Historical.**—During the last thirty years there has been a general belief that the valency linkages of atoms were in some way connected with the electrons of the atom. The fact that polar compounds (§§ 116, 157) can by split up into positively- and negatively-charged ions suggested that the mechanism of chemical combination was the loss by one atom or group of certain electrons and the retention of these by the other atom or group; the first atom was thus positively charged and the second negatively, these charged atoms being then held together by electro-static attraction,

$$A + B = A^+ + B^- = [A]^+[B]^-.$$

As soon as the arrangement of the outer electronic orbits of the atom became cleared up, the way was paved for a more complete theory of valency. The first theory, put forward by Kossel in 1916, satisfactorily explains the formation of ionised compounds—the alkalis and salts, but does not explain the covalent linkages of ordinary compounds.

**153. Electrovalency.**—The inert gases of Group 0 have a peculiarly stable electronic structure characterised by a complete outer group of eight electrons (in the case of helium, two). The elements of Groups I. A, II. A etc., are known to be strongly electro-positive, *i.e.*, they readily lose an electron and become positively-charged ions such as $K^+$, $Mg^{++}$, etc. It is evident from the valencies of the groups of the periodic table that the atoms of the normal elements [1] of the earlier groups readily lose electrons, and in each case revert to the *external structure of an inert gas*, as the table below shows. Just in the same way the elements at the other end of a period (Groups VI., VII.) readily become electro-negative ions, *i.e.*, their atoms *gain* electrons, and their valencies also show that when they do this they reach the type of an inert gas.

The table on p. 186 illustrates the fact that the ions of these elements have the same arrangement of electrons as inert gases. They are not *identical* with the inert gases, because (*a*) they are electrically charged, (*b*) they have a different nuclear charge, and the forces binding the electrons are therefore of different strengths. It is supposed that when a polar compound is formed between such elements as these the process is:

(1) A transference of electrons from the electropositive to the electro-negative atom.

| Na | + | Cl | = | $Na^+$ | + | $Cl^-$ |
|---|---|---|---|---|---|---|
| (2 . 8 . 1) | | (2 . 8 . 7) | | $(2 . 8)^+$ | | $(2 . 8 . 8)^-$ |
| | | | | Neon type. | | Argon type. |

[1] See p. 187 for transition elements.

| Atomic Structure of | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Element. | | | | | | Ion. | | | | | | Corresponding Inert Gas. | | | | |
| Symbol. | +ve Nuclear Charge. | Number of Electrons of | | | | Symbol | +ve Nuclear Charge. | Number of Electrons of | | | | Symbol. | +ve Nuclear Charge. | Number of Electrons of | | | |
| | | 1 quantum | 2 quanta | 3 quanta | 4 quanta | | | 1 quantum | 2 quanta | 3 quanta | 4 quanta | | | 1 quantum | 2 quanta | 3 quanta | 4 quanta |
| Li | 3 | 2 | 1 | — | — | $Li^+$ | 3 | 2 | — | — | — | He | 2 | 2 | — | — | — |
| Mg | 12 | 2 | 8 | 2 | — | $Mg^{++}$ | 12 | 2 | 8 | — | — | Ne | 10 | 2 | 8 | — | — |
| Al | 13 | 2 | 8 | 3 | — | $Al^{+++}$ | 13 | 2 | 8 | — | — | Ne | 10 | 2 | 8 | — | — |
| Cl | 17 | 2 | 8 | 7 | — | $Cl^-$ | 17 | 2 | 8 | 8 | — | A | 18 | 2 | 8 | 8 | — |
| S | 16 | 2 | 8 | 6 | — | $S^{--}$ | 16 | 2 | 8 | 8 | — | A | 18 | 2 | 8 | 8 | — |
| Br | 35 | 2 | 8 | 18 | 7 | $Br^-$ | 35 | 2 | 8 | 18 | 8 | Kr | 36 | 2 | 8 | 18 | 8 |

FIG. 58.

(2) The binding of these charged ions into a solid crystal by electrostatic attraction :

$$Na^+ + Cl^- = [Na]^+[Cl]^-.$$

This theory of valency accounts for the following facts about the combination of the elements (other than transition elements) :

(1) That certain compounds are readily split up into ions.

(2) That the charge on these ions is equal to the number of places by which the element is distant in the periodic table from the nearest inert gas.

In the case of the transition elements electrons may be lost from the *two* outer quantum-groups, and in general the number so lost is not more than three, for it does not seem possible for an ion to exist with more than four charges, and even the latter figure is rare. Consequently the ions of the transition elements do not conform to an " inert gas " pattern but only to a pattern more stable than that of the original atom. Thus transition elements often have variable valency, since there is no outstanding pattern of stability to which they conform. Thus, compare the charges on the ions of the normal and the transition elements of the first long period. It will be seen that in general the only elements which can form two stable ions of different charge belong to the transition grouping. (Copper has a structure analogous to a transition element in many respects.)

**154. Covalent Linkages.**—The majority of compounds—for the organic compounds alone easily outnumber the remainder—are not bound by ionisable linkages. It is not possible to apply the theory we have already outlined to such compounds as, say, sulphur dioxide $SO_2$, or molecular oxygen $O_2$. There is no reason why one atom of oxygen should lose two electrons to the other. To reach the inert gas type, oxygen should gain two electrons or lose six, and the only oxygen molecule one might expect would be

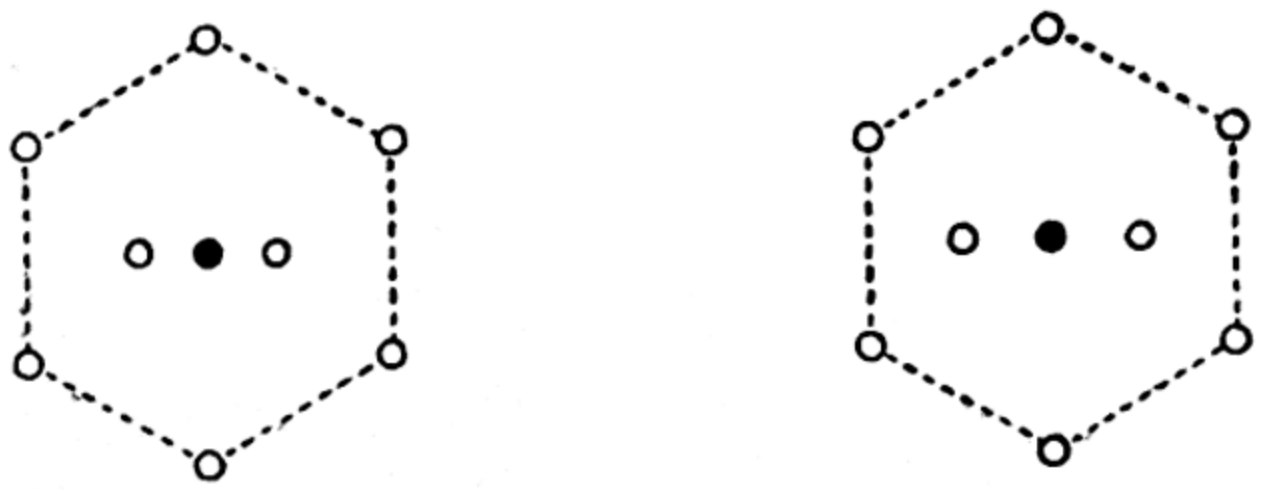
$$\begin{matrix} [o]^{--} & [o]^{--} \\ & [o]^{++++++} \\ & [o]^{--} \end{matrix}$$

or $O_4$, a most improbable arrangement which, in fact, does not occur.

G. N. Lewis propounded, in 1916 a theory of valency which applies to non-ionisable compounds. His principle was that :

In a non-ionisable linkage electrons could be *shared* between two atoms so as to contribute towards the stability of both by bringing their structure to the inert gas pattern.

Thus, consider two atoms of oxygen. Their structure may be diagrammatically represented thus :



If these two could share two of their electrons we should have

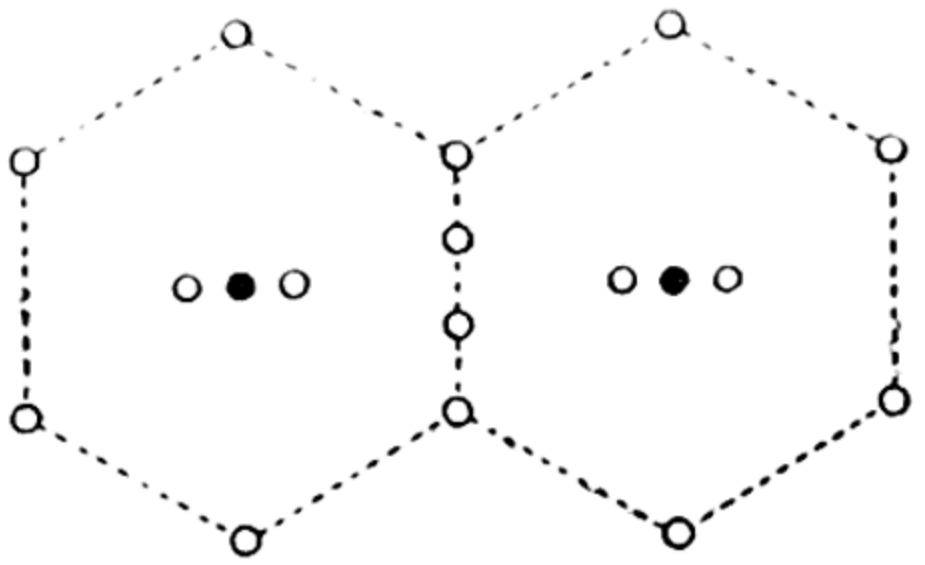
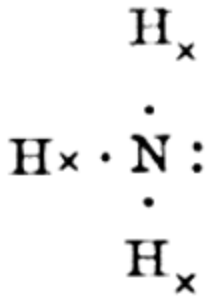


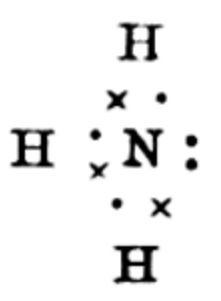
FIG. 59.

in which each atom has eight electrons in its outer quantum-group, a state of affairs which is an approximation to the inert gas pattern.

Again consider the formation of a molecule of ammonia from three atoms of hydrogen and one atom of nitrogen. The latter atom shares three electrons, which with its original five brings it to the stable neon-type. The hydrogen atoms each share one of the nitrogen atom's electrons, thus reaching the helium-type.



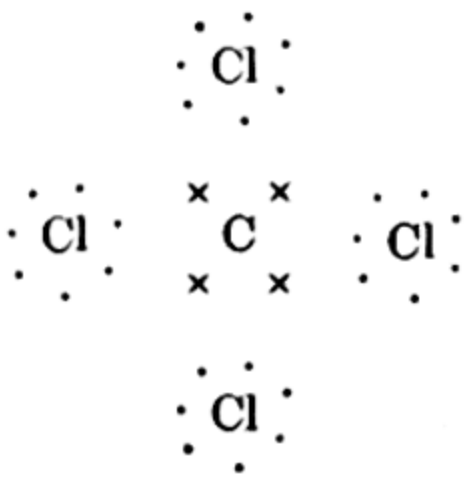
Three hydrogen atoms with 1 electron ( × ) each. One nitrogen atom with 5 electrons ( . ) in outer ring.



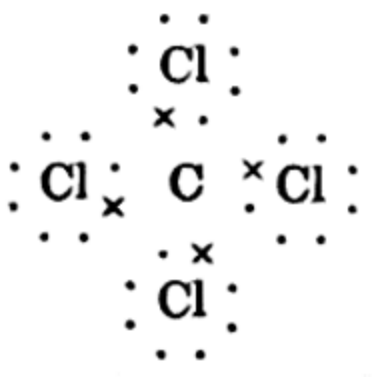
Molecule of ammonia. The hydrogen atoms have a complete 2-ring (helium-type) and the nitrogen atoms a complete 8-ring (neon-type).

By sharing electrons, two atoms, both of which have two electrons too few for stability, can each gain a stable outer layer of eight electrons. This type of combination will therefore occur briefly in the case of elements which have too few electrons for the inert gas pattern, *e.g.*, Groups IV. to VII., not in the case of those elements which have too many electrons, Groups I. to III. Thus we find the electronegative elements (non-metals) form covalent—non-ionisable—compounds much more readily than do the electropositive elements —metals.

We may often represent these linkages diagrammatically by showing the outer electrons only. Thus carbon tetrachloride may be represented (showing the electrons derived from the carbon as × and those from the chlorine as .).




Carbon atom and chlorine atoms have incomplete outer rings of 4 and 7 electrons respectively.

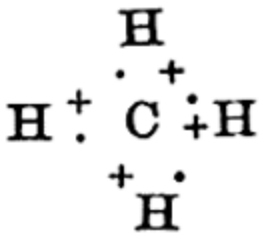



In carbon tetrachloride every atom is encircled by 8 electronic orbits.

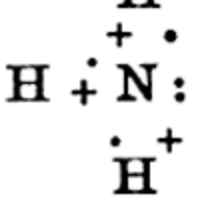
These covalent linkages are not broken up by ionisation, because the atoms or groups are actually held together by two or more encircling electronic orbits and because there is not a marked difference of polarity between the different parts of the molecule.

**155. Co-ordinate Linkages.**—The covalent linkage comes about by the sharing of a pair of electrons, *one from each atom*. If both electrons are contributed by one atom then the co-ordinate type of linkage results. For an atom to form such a linkage it must have a pair of electrons unshared by any other atom.

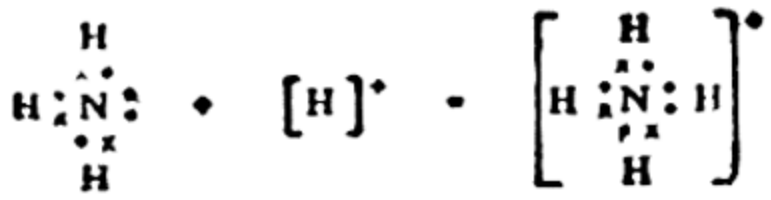
Thus methane



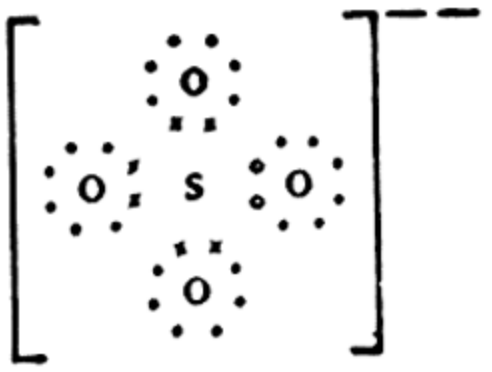
could not form such a linkage, for all its electrons are shared ; but ammonia



can form such compounds (§ 692). Thus with hydrogen ion (acids) it forms the ammonium ion.

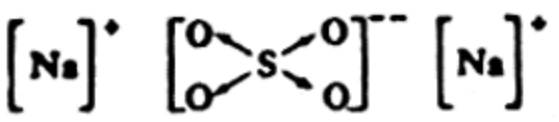


The hydrogen ion, destitute of electrons, shares nitrogen's spare pair, so becoming of the helium type. In doing this the ion receives the positive charge of the hydrion. Again, in the sulphate ion the sulphur and oxygen do not contribute equal numbers of electrons. If they did so the product would be SO. Actually, the sulphur contributes all its electrons to the oxygen, receiving none in return, and since it has only six of these the eight are made up by taking two from outside.



. Electrons from O atoms.
× Electrons from S atoms.
° Electrons from outside.

A co-ordinate linkage is represented by an arrow —→ pointing towards the atom receiving the electrons. Thus sodium sulphate is



It must be noted that the co-ordinate linkage differs from the ordinary covalent linkage only in the way in which it is formed. The final result is

the same : thus in the ammonium ion all four hydrogen atoms are attached with precisely the same strength, symmetrically, and at the same distance.

Molecular compounds, such as the ammines, hydrates, etc., are probably joined by co-ordinate linkages. Complications are introduced by the fact that the octet of outer electrons is not the only possibility, a set of twelve electrons having the same features of stability. The co-ordinate linkage is further discussed under metallic ammines.

**155a. Resonance.**—Every linkage between atoms need not necessarily be of one of the above types only, for in many cases they can be of an intermediate or mixed character. Where the atoms of a molecule could be represented as being linked by two of the above types of valency, it is common to find that the linkage has some of the characters of both types, owing the phenomenon of resonance that follows from wave-mechanics. Thus hydrogen fluoride behaves in some ways as H—F (covalent) and in other ways as $H^+F^-$ (electrovalent); it does not behave as a mixture of two forms, but as intermediate in character between what would be expected of a compound of formula (covalent) H—F and one of formula $H^+F^-$.

**156. Summary.**—To summarise, there are three types of valency :—

(1) *Electrovalency.* This is the result of a passage of electrons from one atom to another, ions being formed. The electrical attraction between these binds the radicals of alkalis and salts.

(2) *Covalency.* This results from the sharing of electrons between two atoms, each atom contributing equal numbers. It is found in the great majority of organic and inorganic compounds other than salts.

(3) *Co-ordinate valency.* This results from an atom contributing two (or very rarely one) electrons to another atom, but itself receiving none. Such linkages are found where apparently saturated compounds unite with atoms or molecules ; they also connect the atoms which build up many of the most important ions (§§ 777, 916, etc.).

It is to be realised, however, that these are extreme cases and that many linkages are intermediate between them.

# CHAPTER VIII

## ACIDS, BASES AND SALTS

**157. The Nature of Acids, Bases and Salts.**—The classification of chemical substances into ionisable and non-ionisable compounds has already been discussed in Chapter VI. It was there pointed out that certain chemical compounds are distinguished from all others by—

(1) The fact that they undergo electrolysis.
(2) Their abnormally low apparent molecular weight in solution.
(3) The additive character of their properties.

These substances are said to be ionisable, and it was shown that these properties and some others were accounted for if it was assumed that the substances were, in part or wholly, dissociated in solution into chargedparticles or ions.

Ionisable compounds are further classified as acids, bases and salts. The exact definition of these has always presented some difficulty owing to the fact that many substances belong to two of these classes. In the later part of the chapter definitions are given which do not involve the use and terminology of the ionic theory, but, at any rate to the more advanced student, the definitions of Brønsted provide the most enlightening classification.

*Acids.—Acids are compounds which ionise to form hydrogen ion* $H^+$. We may represent this definition by the equation

$$HA \rightleftharpoons H^+ + A^-.$$
Acid. Hydrogen ion.

*Bases and Alkalis.*—An alkali is often defined as *a substance which ionises in aqueous solution to form hydroxyl ion* $OH^-$. On this system the definition of an alkali is given by

$$BOH \rightleftharpoons OH^- + B^+.$$
Base. Hydroxyl ion.

The definition of a base is, however, much wider in scope, and a base may be properly defined as *a substance which reacts with hydrogen ion* or as a *proton-acceptor*. This definition includes all types of base. Thus alkalis are included

$$B.OH \rightleftharpoons OH^- + B^+$$
$$OH^- + H^+ = H_2O.$$

and also basic metallic oxides such as copper oxide

$$CuO + 2H^+ = Cu^{++} + H_2O.$$

Such substances as ammonia or aniline are also covered by this definition.

$$NH_3 + H^+ = NH_4^+$$
Ammonia. + Hydrion. Ammonium ion.

$$C_6H_5NH_2 + H^+ = C_6H_5NH_3^+.$$
Aniline. + Hydrion. Anilinium ion.

In this definition of a base there is one point which could cause some doubt. If a base is a substance which combines with hydrion, then such substances as the acetate ion $CH_3 . COO^-$ must be regarded as bases, for they undoubtedly combine with hydrion, *e.g.*,

$$CH_3 . COO^- + H^+ \rightleftharpoons CH_3 . COOH$$

It is to-day generally regarded as reasonable to extend the term base to such ions, the behaviour of which is certainly analogous to that of ordinary bases, such as ammonia, etc.

*Salts* are to be regarded as compounds which, when they ionise, do not give hydrogen ion as the sole positive product nor hydroxyl ion as the sole negative product. Thus copper chloride and sodium hydrogen sulphate are both salts.

$$[Cu]^{++}[Cl]_2^- \rightleftharpoons Cu^{++} + 2Cl^-$$
$$[Na]^+[HSO_4]^- \rightleftharpoons Na^+ + HSO_4^- \rightleftharpoons Na^+ + H^+ + SO_4^{--}$$

## ACIDS

**158. Historical.**—The only acid known to the ancients was vinegar (Lat., *acetum* ; Greek, *ὄξος*, *oxos*). It was recognised that vinegar, unripe fruits, etc., had in common the taste to which we give the name "sour" (Lat., *acidus* ; Greek, *ὀξύς*, *oxys*). The Greek alchemists (*c.* A.D. 100–800) made great use of vinegar and extended the use of the word *ὄξος* till it meant any corrosive liquid. It was then natural that when nitric and sulphuric acid (*q.v.*) were discovered they should be regarded as sour substances like vinegar, *i.e.*, acids.

Lavoisier, who knew that most of the oxides of the non-metallic elements dissolved in water, forming acids, concluded that all acids contained oxygen, and even named oxygen[1] from this property.

The discovery of the constitution of such acids as hydrochloric acid HCl, hydriodic acid HI, hydrocyanic acid HCN, soon made this theory untenable, and the modern hydrogen theory of acids took its place.

[1] *ὀξύς*, *oxys*, sour; *γεννάω*, *gennao*, I produce.

**159. Definition of an Acid.**—The best and simplest definition of an acid is the simple statement that

**Acids are compounds which ionise to form hydrogen ion $H^+$.**

It must be remembered, however, that weak acids yield extremely low concentrations of hydrion and their solutions may not display any of its more obvious properties. It is well, then, also to retain the older definition which states that **an acid is a compound containing hydrogen, which may be partly or wholly replaced by a metal, when a solution of the compound is treated with certain metallic oxides or hydroxides, such as those of the alkali metals; a salt and water being the only products.**

We may express this definition symbolically by saying that an acid is a substance, $H_n(X)$, which undergoes the transformation,

$$H_n(X) + m\text{NaOH} = \text{Na}_m H_{n-m}(X) + m H_2O$$

when it is treated with a solution of caustic soda.

**160. Constitution of Acids.**—All acids contain hydrogen, and this hydrogen is linked to a comparatively electronegative atom or group in such a way as to be readily separated from it. Thus the great majority of the reactions of such an acid as sulphuric acid, $H_2SO_4$, result in the separation of the hydrogen atoms from the $= SO_4$ group. Electrolysis splits up the acid in this way, as also does treatment with alkalis and metals. Electrolytic dissociation produces hydrogen ions and sulphate ions. From these and similar facts it may be concluded that acids consist of two readily separable parts, *hydrogen* and an *acid radical*. These are shown in the list below separated by lines representing the valency linkages.

| Acid. | Hydrogen — Acid radical |
|---|---|
| Sulphuric acid | $H_2 = SO_4$ |
| Nitric acid | $H - NO_3$ |
| Hydrochloric acid | $H - Cl$ |
| Phosphoric acid | $H_3 \equiv PO_4$ |
| Acetic acid | $H - C_2H_3O_2$ |

Studies of the shape and dimensions of molecules have shown that the hydrogen and the acid radical are covalently linked in absence of water but that in presence of water this linkage breaks and ions are formed. As mentioned below the hydrion combines with water forming hydroxonium ion $H_3O^+$. Thus hydrogen chloride gas has the molecular structure

$$H : \ddot{\underset{\cdot\cdot}{Cl}} :$$

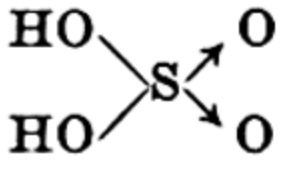
and in presence of water it reacts thus:

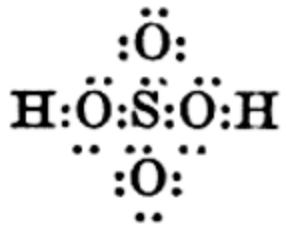
$$H_2O + H : \ddot{\underset{\cdot\cdot}{Cl}} : \rightarrow \left[H_3O\right]^+ + \left[: \ddot{\underset{\cdot\cdot}{Cl}} :\right]^-$$

Strong acids are completely dissociated, but weak acids undergo an equilibrium reaction, *e.g.*,

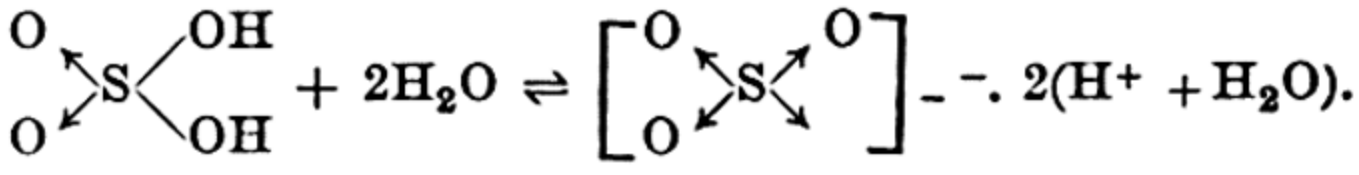
$$H_2O + H:\ddot{F}: \rightleftharpoons \left[H_3O\right]^+ + \left[:\ddot{F}:\right]^-$$

Again. anhydrous sulphuric acid is probably wholly linked by covalency and has the formula





but on addition of water the acid ionises thus :—



It will be noted that anhydrous sulphuric acid has not the usual properties of an acid.

**161. Physical Properties of Acids.**—The general properties of acids in solution are those of *hydrion* $H^+$, which is formed by the ionic dissociation of all acids.

Actually, in fact, the greater part of the hydrion combines with water forming $H_3O^+$ (or $H^+.H_2O$), and it is this hydroxonium ion which is referred to when hydrion is spoken of. The formula $H^+$ is, however, still commonly used.

$$HCl \rightleftharpoons H^+ + Cl^-$$
$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$$
$$HCN \rightleftharpoons H^+ + CN^-.$$

Acids, in general, have a sour taste. This is a property of hydrion. Strong acids which furnish much hydrion have a very sour taste, and as little as one part of acid per million may be detected in this way. Such acids, however, as hydrogen sulphide, boric and carbonic acids, which are ' weak ' acids, and only dissociate to a very small extent, have little or no sour taste.

Acids are always, to some extent, soluble in water and usually dissolve freely. Their solutions conduct electricity. Solutions of strong acids are good conductors for two reasons. They contain a large concentration of ions to carry the current, and the hydrion produced by them is particularly effective in doing so on account of the comparatively high velocity with which it moves through the liquid. This high velocity results in a solution of hydrion being about six times as conductive as an equivalent solution of any other ion.

The hydrion moves so rapidly, it is thought, because it is present as the hydroxonium ion $H^+ . H_2O$, the proton of which is *handed on* from one water molecule to the next, instead of having to push its way amongst the water molecules, as do other ions.

**162. Electrolysis of Acids.**—When acids carry the electric current they are decomposed (Chapter VI.) The hydrions wander to the negative pole or cathode and the acid radical ions to the positive pole or anode. As they reach these they give up their charges, and free hydrogen and acid radical are liberated.

$$HX \rightleftharpoons H^+ + X^- ;\ H^+ + \ominus = H ;\ X^- = X + \ominus.$$

Secondary reactions usually occur at the anode and sometimes at the cathode.

*Reactions at the Cathode.*—At the cathode the hydrogen atoms usually combine and come off as hydrogen gas,

$$H + H = H_2,$$

but occasionally the hydrogen reduces the acid. Thus the electrolysis of nitric acid results in hydrogen, which then reacts with more of the acid and forms a variety of products, which may include ammonia $NH_3$, hydroxylamine $NH_2OH$, hyponitrous acid $H_2N_2O_2$, nitrogen, nitrous oxide, nitrous acid, etc., as a result of such reactions as

$$HNO_3 + 8H = NH_3 + 3H_2O,$$

or

$$HNO_3 + 6H = NH_2OH + 2H_2O, \text{ etc.}$$

*Reactions at the Anode.*—The discharged ion of the acid radical may be a single atom, Cl, Br, I or a group, CN, $SO_4$, $NO_3$, $C_2H_3O_2$, etc.

In the first case the element is produced.

$$Cl + Cl = Cl_2,$$

and is evolved if neither the solution nor anode is attacked by it.

No group of atoms can function as an acid radical and also exist free, for there must be an unsatisfied valency bond to which the acidic hydrogen was originally linked. Such groups as $SO_4$, $NO_3$, are not at all readily discharged at the anode and the $OH^-$ group which is always present in water is discharged instead.

Thus when a solution of a sulphate is electrolysed in a cell with a platinum anode the sulphate ions travel to the anode and so carry the current, but they are not discharged there. Hydroxyl ions from the water are discharged

$$2OH^- \rightarrow H_2O + \mathbf{O} + \ominus$$
$$\mathbf{O} + \mathbf{O} = O_2\uparrow.$$

Water is in chemical equilibrium with $H^+$ and $OH^-$ ions, so as the latter are removed fresh ones take their place,

$$H_2O \rightleftharpoons \underset{\text{Hydrion}}{H^+} + \underset{\text{Hydroxyl ion}}{OH^-}$$

The hydrions accumulate round the anode together with the sulphate ions, constituting a solution of sulphuric acid.

Other secondary reactions may take place. Thus the acetate group when liberated forms ethane and carbon dioxide,

$$2C_2H_3O_2 = C_2H_6 + 2CO_2.$$

Other examples of secondary reactions are to be found in § 946. If the anode is of a metal readily attacked by reagents, the acid radical attacks and dissolves it.

Thus, if the sulphate group be liberated at a zinc pole, the reaction

$$SO_4 + Zn = ZnSO_4$$

takes place and zinc sulphate is formed (cf. § 27). It may be helpful to give one or two examples of the electrolysis of acids.

*Electrolysis of Hydrochloric Acid.*—Hydrogen and chlorine are formed.

$$\mathbf{HCl}$$
$$\rightleftarrows$$
$$H^+ + Cl^-$$

$-$ Cathode: $H^+ + \ominus = H \uparrow$, $H + H = \mathbf{H_2} \uparrow$

$+$ Anode: $Cl^- = Cl + \ominus \uparrow$, $Cl + Cl = \mathbf{Cl_2} \uparrow$

*Electrolysis of Sulphuric Acid.*—Hydrogen and oxygen are formed, water is decomposed, and sulphuric acid collects round the anode.

$$\mathbf{H_2SO_4}$$
$$\rightleftarrows$$
$$2H^+ + SO_4^{--}$$

$-$ Cathode: $2H^+ + 2\ominus = 2H = \mathbf{H_2}$

$+$ Anode: $SO_4^{--} + 2H^+ \rightleftharpoons \mathbf{H_2SO_4}$

$2H_2O \rightleftharpoons 2H^+ + 2OH^-$

$2OH^- \rightarrow H_2O + O + \ominus$

$O + O \rightarrow \mathbf{O_2}$

**163. Chemical Properties of Acids.**—The chemical properties common to all acids are those of hydrion $H^+$ : individual differences are due to reactions of the undissociated acid or the other ions.

Few acids react with the non-metallic elements ; if any do so it is on account of the oxidising properties of the acid radical or undis-

sociated acid, as in nitric, chromic, sulphuric acids (§§ 743, 936). With certain of the metals, however, acids react, forming salts and hydrogen. In general, it may be said that the metals less electropositive than hydrogen react with ordinary acids in this way. These include the metals lying between and including potassium and tin in the electrochemical series (§ 126). The presence of resistant surface films of oxide may modify this rule.

The general reaction is

$$M + nH^+ = M^{n+} + nH$$

$$nH = \frac{n}{2} H_2$$

But since in the laboratory we weigh out and measure acids and not hydrion we require the chemical equations for the reaction of individual metals and acids, *e.g.*,

$$Zn + 2HCl = ZnCl_2 + H_2,$$
$$Mg + H_2SO_4 = MgSO_4 + H_2.$$

Certain oxidising acids, such as nitric acid, react in a different manner and form other products (§ 744).

Acids react with many of the oxides of metals, forming salts and water only. Oxides which react in this way are called basic oxides. The oxides of the non-metallic elements do not react with acids. Thus magnesium oxide and hydrochloric acid yield magnesium chloride and water.

$$MgO + 2H^+ = Mg^{++} + H_2O$$

*or*

$$MgO + 2HCl = MgCl_2 + H_2O.$$

Ferric oxide and sulphuric acid give ferric sulphate and water,

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O.$$

The equations are easily written if it is remembered that the hydrogen of the acid and the oxygen of the oxide together form water.

The hydroxides of the metals are also converted into salts and water when treated with acids. This reaction is simply the combination of hydrion and hydroxyl ion (§§ 117, 167)

$$H^+ + OH^- = H_2O.$$

Thus sodium hydroxide and acetic acid give sodium acetate and water,

$$NaOH + C_2H_4O_2 = NaC_2H_3O_2 + H_2O,$$

and cupric hydroxide and hydrochloric acid give cupric chloride and water,

$$Cu(OH)_2 + 2HCl = CuCl_2 + 2H_2O$$

Acids do not react with each other, unless oxidation or reduction takes place, cf. p. 697(8), but acids react with salts according to the general equation,

$$HA + BC \rightleftharpoons HC + BA.$$

Thus a solution of an acid will always displace another acid from its salts *to some extent*. Whether the reaction is of *practical* value depends on the extent of the transformation and also on the volatility or solubilities of the products.

If we treat the process by the ionic theory we shall see the conditions more clearly. The acid HA will be ionised to some extent and the salt, BC, will be completely dissociated.

$$(1)\ HA \rightleftharpoons H^+ + A^-.$$
$$(2)\ BC \rightleftharpoons B^+ + C^-.$$

The four ions formed will react, forming the acid HC, and the salt BA.

$$(3)\ B^+ + A^- \rightleftharpoons BA.$$
$$(4)\ H^+ + C^- \rightleftharpoons HC.$$

If HA is a strong acid it will form a great deal of hydrion, and this will combine with $C^-$ (eq. 4), and form a good deal of the acid HC; but if HA is a weak acid very little hydrion will be formed (eq. 1), and so very little of the acid HC will be formed (eq. 4) *unless* the acid HC is removed as fast as it is formed, which may happen if it is insoluble in water or unstable or volatile; in this case the reaction will go to completion.

**164. Preparation of Acids.**—(i.) *From an Acid and a Salt.*—This last-mentioned process indicates one of the chief ways of making an acid. *An acid may be made from its salts by the action of another acid if either the acid to be prepared or another reaction product can be removed from the reaction mixture by volatilisation or precipitation.*

As a first example we may take the preparation of nitric acid (§ 735). When a nitrate is mixed with concentrated sulphuric acid the reaction

$$H_2SO_4 + KNO_3 \rightleftharpoons KHSO_4 + HNO_3$$

occurs. If the mixture is heated the nitric acid boils off at about 85° C. and the equilibrium is only restored by more nitrate and acid reacting. Thus the reaction goes to completion. The nitric acid vapour is condensed and the acid obtained in a comparatively pure state.

Acids prepared by methods similar to this include perchloric and hydrochloric acids, acetic, formic, hydrocyanic and many other organic acids.

As a second example we may take the preparation of boric acid. A solution of sodium diborate (borax) is mixed with concentrated

hydrochloric acid and diboric acid is formed according to the first equation below :

$$Na_2B_4O_7 + 2HCl \rightleftharpoons H_2B_4O_7 + 2NaCl$$
$$H_2B_4O_7 + 5H_2O = 4H_3BO_3 \downarrow$$

This diboric acid combines with water and forms orthoboric acid, which is sparingly soluble in water and crystallises out.

A third type of method for preparing acids is particularly useful for unstable acids. A solution of a salt formed from the acid and a metal is treated with another acid which forms an insoluble salt with that metal. The salt is filtered off and the acid required remains in solution. Thus a solution of barium chlorate may be treated with the exact quantity of sulphuric acid required by the equation,

$$Ba(ClO_3)_2 + H_2SO_4 = 2HClO_3 + BaSO_4. \downarrow$$

The barium sulphate is filtered off and chloric acid remains in solution.

(ii.) *From Acidic Oxides and Water.*—Another general method of preparing acids is by the action of acidic oxides on water.

The method is not of very great importance but is used in the preparation of carbonic, sulphurous, sulphuric and phosphoric acids.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3,$$
$$SO_3 + H_2O = H_2SO_4.$$

(iii.) *The action of Halides on Water.*—Acid chlorides[1] and some chlorides of non-metals yield, when treated with water, an oxyacid of the element in question and hydrochloric acid. Thus phosphorous acid may be made by the action of phosphorus trichloride on water,

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

## BASES AND ALKALIS

**165. Definitions of Bases and Alkalis.**—According to modern definitions **a base is a substance which reacts with hydrogen ion.**

Such compounds include

(1) The oxides of most metals

$$MgO + 2H^+ = Mg^{++} + H_2O$$

(2) The hydroxides of nearly all metals and, of course, hydroxyl ion itself

$$NaOH + H^+ = Na^+ + H_2O$$

[1] Substances obtained when a hydroxyl group present in the covalent form of an acid is replaced by chlorine. Thus sulphuric acid $SO_2(OH)_2$ by treatment with phosphorus pentachloride is converted into the *acid chloride* sulphuryl chloride $SO_2Cl_2$. Treated with water, this substance yields sulphuric acid.

(3) Ammonia and amines

$$NH_3 + H^+ \rightarrow NH_4^+$$
$$C_6H_5NH_2 + H^+ \rightarrow C_6H_5NH_3^+.$$

According to the older definition, which excludes the last class, a base is a substance which reacts with acids forming a salt and water only. Bases, so defined, must be compounds of metals or electro-positive groups with oxygen or hydroxyl. Such compounds include

(1) Most metallic oxides :

$$MgO + H_2SO_4 = MgSO_4 + H_2O,$$
$$Ag_2O + 2HNO_3 = 2AgNO_3 + H_2O.$$

(2) Nearly all metallic hydroxides :

$$NaOH + HCl = NaCl + H_2O,$$
$$2Al(OH)_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 6H_2O,$$
$$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O.$$

The basic metallic hydroxides which are soluble in water are termed *alkalis* (*v. infra*). The majority of such hydroxides are insoluble in water and are to be regarded as bases only.

*Alkalis.*—**Alkalis are basic hydroxides soluble in water.** It follows then that all alkalis are bases, but that many bases (*e.g.*, oxides and hydroxides of the 'heavy metals') are not alkalis. By ionic dissociation they yield the $OH^-$ group, hydroxyl ion, and it is to this that their common properties are to be attributed.

$$NaOH \rightleftharpoons Na^+ + OH^-,$$
$$Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH^-.$$

**166. Reaction of Bases with Water.**—The oxides of the alkali metals and alkaline earths react vigorously with water, forming the hydroxides of these elements.

$$Na_2O + H_2O = 2NaOH,$$
$$CaO + H_2O = Ca(OH)_2.$$

The majority of metallic oxides are, however, only very slightly soluble in water, and in so far as they dissolve they appear to form hydroxides (see above).

**167. Reaction of Acids and Bases—Neutralisation.**—It is not certain whether the reaction between basic oxides and acids is ionic or whether it takes place between the oxide and the undissociated acid molecules, *i.e.*,

$$CuO + 2H^+ + 2Cl^- = Cu^{++} + H_2O + 2Cl^-.$$

*or* $$CuO + 2HCl = CuCl_2 + H_2O \rightleftharpoons Cu^{++} + H_2O + 2Cl^-$$

In all cases a salt and water is formed. The reactions are sometimes very slow, particularly with such oxides as those of iron, chromium and aluminium.

When an acid reacts with an alkali, both being in solution, the reaction is almost instantaneous.

Since in dilute solution strong acids and alkalis are wholly ionised, and since the characteristic properties of acids and alkalis are due to hydrion and hydroxyl ion respectively, it is only these ions which take part in the reaction. Thus the reaction we ordinarily write as

$$NaOH + HCl = NaCl + H_2O$$

is really

$$Na^+ + OH^- + H^+ + Cl^- = Na^+ + Cl^- + H_2O$$

or

$$OH^- + H^+ = H_2O.$$

Now, if we had substituted in our argument any other alkali or acid for caustic soda and hydrochloric acid, we should still find that the equation came finally to the same

$$OH^- + H^+ = H_2O.$$

The hydroxyl and hydrogen ions combine and form water, while the ions of the acidic and basic radicals simply remain in solution.

This view of neutralisation is supported by the fact that when an equivalent of *any* well-diluted strong acid neutralises an equivalent of *any* strong base, 13,700 calories of heat are produced.

Now it is well known that different reactions produce different quantities of heat (§ 27), and we must conclude that all neutralisations of acids by alkalis are the same reaction, *i.e.*,

$$H^+ + OH^- = H_2O + 13{,}700 \text{ cals.}$$

The matter is further discussed in § 117.

**168. General Properties of Bases and Alkalis.**—The alkalis are, of course, soluble in water. They have a peculiar soapy taste, and the strongest alkalis have a slippery feeling when rubbed between the fingers.

Their solutions are, for the most part, completely dissociated. Thus sodium hydroxide both in the solid state and in solution consists entirely of $Na^+$ and $OH^-$.

Ammonia, however, which is a weak base, reacts with water and forms a proportion of ammonium and hydroxyl ions.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-.$$

When alkalis are electrolysed the electropositive ion travels to the cathode, while the hydroxyl ion is discharged at the anode.

*Reactions at Cathode.*—The positive ions travel to the cathode, so carrying the current. The ions of the metals which form soluble hydroxides are very stable and not easily discharged consequently, the hydrion present in the water is discharged in preference. Its place is supplied by more water dissociating

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$2H^+ \rightarrow H_2$$

Hydroxyl ion therefore accumulates and with the metallic ion forms a solution of the alkali round the cathode.

*Reaction at Anode.*—At the anode the hydroxyl group reacts with itself, forming oxygen and water.

$$OH + OH = H_2O + O$$
$$O + O = O_2 \uparrow$$

Thus oxygen and hydrogen are the only products and the alkali accumulates round the cathode.

As an example we may take the electrolysis of barium hydroxide solution.

$$\mathbf{Ba(OH)_2}$$
$$\Downarrow\Uparrow$$
$$Ba^{++} + 2OH^-$$

$-$ Cathode

$$\mathbf{Ba^{++}} + \mathbf{2OH^-}$$
$$\uparrow$$
$$2H_2O \rightleftharpoons 2H^+ + 2OH^-$$
$$2H^+ \rightarrow \mathbf{H_2}\uparrow + 2\ominus$$

$+$ Anode

$$2OH^- = 2OH + 2\ominus$$
$$2OH = H_2O + O$$
$$O + O = \mathbf{O_2}\uparrow$$

The electrolysis of fused alkalis, water not being present, results in the production of the metal (§ 223).

The reactions between bases and acids have already been discussed (§ 167).

Alkalis and salts frequently react; the solution of alkali contains hydroxyl ion which may form an insoluble hydroxide with the metallic ions of the salt.

A base is best defined as a compound which reacts with hydrion. All metallic hydroxides are insoluble in water except those of the alkali metals, alkaline earths and thallium, and, accordingly, on mixing a solution of an alkali with a solution of a salt of one of the heavy metals a precipitate of the hydroxide of the metal

is obtained. Thus with any copper salt and any alkali, insoluble cupric hydroxide is precipitated,

$$Cu^{++} + 2OH^{-} = Cu(OH)_2,$$

In each particular case we may write a full equation, which may be useful to indicate the quantities to be used in practical work. Thus when copper sulphate and potassium hydroxide give potassium sulphate and copper hydroxide the equation is

$$CuSO_4 + 2KOH = K_2SO_4 + Cu(OH)_2\downarrow,$$

Occasionally the oxide is obtained where the hydroxide is unstable (§§ 306, 329, 443).

Ammonium hydroxide is unstable; and consequently when an ammonium salt is heated with an alkali, ammonia gas is formed (§ 691).

**169. Preparation of Alkalis and Bases.**—Alkalis are, in general, made :—

(1) By the action of water on the oxides of the alkali metals (sodium, potassium, etc.), or of the metals of the alkaline earths (calcium, strontium, barium),

$$Na_2O + H_2O = 2NaOH$$
$$BaO + H_2O = Ba(OH)_2.$$

(2) By the action of water on the metals of the above classes. The metals are often formed by electrolysis and at once allowed to decompose water, cf. § 230.

$$2K + 2H_2O = 2KOH + H_2$$
$$Ca + 2H_2O = Ca(OH)_2 + H_2.$$

(3) By double decomposition. Thus sodium hydroxide may be made by the action of sodium carbonate on calcium hydroxide.

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3\downarrow + 2NaOH.$$

The removal of the insoluble calcium carbonate by precipitation causes the reaction to complete itself.

The methods are more fully discussed under the heading of the individual alkalis.

## SALTS

**170. Definition and Constitution of Salts.**—The term salt (Latin *sal*, Greek ἅλς, *hals*) was in ancient times applied to common salt. The term was extended in the Middle Ages to substances resembling common salt in appearance, solubility, etc. (*e.g.*, potassium nitrate, ammonium chloride).

From the point of view of the chemist a salt is a compound formed from an acid by replacement of a part or the whole of its hydrogen by a metal or basic radical.

A salt, then, consists of *basic radicals* and *acidic radicals*. Most true salts are wholly dissociated into ions both in the solid state and in solution, and these ions consist of the acidic and basic radicals with a negative and positive charge respectively ; the charge on each ion being that of a number of electrons equal to its valency.

The structure of the molecules of salts is discussed in §§ 103, 153, 155.

**171. Types of Salt.**—Three chief types of salts are distinguished, *normal salts*, *acid salts* and *basic salts*.

*Normal salts* contain neither replaceable hydrogen nor replaceable oxygen or hydroxyl. When a normal salt is formed *all* the replaceable hydrogen of the acid combines with *all* the replaceable oxygen or hydroxyl of the base. Thus copper sulphate $CuSO_4$ is a normal salt, as also are the salts numbered 1, 2, and 5 in the list given below.

*Acid salts* contain replaceable hydrogen and are formed when a polybasic acid reacts with a quantity of a base insufficient to replace the whole of the replaceable hydrogen.

Sodium hydrogen sulphate $NaHSO_4$ is an acid salt, as are also sodium bicarbonate $NaHCO_3$, calcium tetrahydrogen phosphate $CaH_4(PO_4)_2$, etc. They have the properties of salts in addition to those of acids.

*Basic salts* contain oxygen or hydroxyl, which is replaceable by an acid radical, a normal salt being formed. Thus bismuth oxychloride BiOCl is a basic salt, for with hydrochloric acid it forms bismuth trichloride,

$$BiOCl + 2HCl \rightleftharpoons BiCl_3 + H_2O.$$

A great many so-called basic salts are merely mixtures of hydroxides and normal salts, as is shown by their variable composition (§ 567).

The following table illustrates the connection between certain acids, bases and salts, and the ions formed from the latter :—

| Salt. | Formed from | | Ions formed by Salt. | |
|---|---|---|---|---|
| | Acid. | Bases. | Electro-positive. | Electro-negative. |
| 1. Sodium chloride $NaCl$ | $HCl$ | $NaOH$, $Na_2O$ | $Na^+$ | $Cl^-$ |
| 2. Calcium nitrate $Ca(NO_3)_2$ | $HNO_3$ | $Ca(OH)_2$, $CaO$ | $Ca^{++}$ | $NO_3^-$, $NO_3^-$ |
| 3. Copper sulphate $CuSO_4$ | $H_2SO_4$ | $Cu(OH)_2$, $CuO$ | $Cu^{++}$ | $SO_4^{--}$ |
| 4. Di-sodium hydrogen phosphate $Na_2HPO_4$ | $H_3PO_4$ | $NaOH$, $Na_2O$ | $Na^+$, $Na^+$ | $HPO_4^{--}$ ($PO_4^{---}$) |
| 5. Ammonium chloride $NH_4Cl$ | $HCl$ | $NH_4OH$ | $NH_4^+$ | $Cl^-$ |
| 6. Uranyl nitrate $UO_2(NO_3)_2$ | $HNO_3$ | $UO_2(OH)_2$, $UO_3$ | $UO_2^{++}$ | $NO_3^-$, $NO_3^-$ |

*Double and Complex Salts.*—Two or more salts often combine, forming what is called a double or complex salt. The term double salt is often applied to such of these as have a well-defined and distinctive crystalline form and other physical properties, but in solution behave chemically like a mixture of the two constituent salts. Their formulæ are commonly written as if the molecules of the two salts combined as wholes, *e.g.* :—

Alum, potassium aluminium sulphate, $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$.

Ferrous ammonium sulphate, $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$.

But though this may sometimes be the case, it is usual for one salt to form a complex anion. Thus the above formulæ are probably better written as

Potassium aluminisulphate, $K[Al(SO_4)_2] . 12H_2O$,

Ammonium ferrosulphate, $(NH_4)_2[Fe(SO_4)_2] . 6H_2O$.

Compounds of two salts are termed *complex salts* if their solutions contain a notable proportion of the complex ion. Alum forms some $Al(SO_4)_2^-$ ion when it dissolves, but this is almost wholly broken up into $Al^{+++}$ and $SO_4^{--}$ ions. Such a salt as potassium ferrocyanide, on the other hand, behaves very differently. Its formula, $K_4Fe(CN)_6$, might be written $4KCN . Fe(CN)_2$, *i.e.*, as potassium ferrous cyanide ; but, in fact, such a formula would be quite misleading, for it has none of the typical properties of the cyanides (hydrolysis to alkalis and hydrocyanic acid, poisonous properties, etc.). Actually, when it ionises it forms $4K^+$ and $[Fe(CN)_6]^{----}$ *not* $4K^+$, $Fe^{++}$ and $6CN^-$.

The majority of double salts are intermediate between the two extreme cases outlined above. Thus, for example, potassium cadmicyanide $K_2Cd(CN)_4$, derived from potassium cyanide KCN and cadmium cyanide $Cd(CN)_2$, gives both cadmicyanide ions, cadmium ions and cyanide ions :

$$K_2Cd(CN)_4 \rightleftharpoons 2K^+ + Cd(CN)_4^{--} \rightleftharpoons 2K^+ + Cd^{++} + 4CN^-.$$

The characterisation of a salt as double, complex or intermediate depends simply on equilibria such as the above.

The equilibrium constant of the reaction between the complex ion and its components is called the *stability constant* of the salt. Double salts have a low stability constant, complex salts a high one.

Thus in the above case

$$[Cd(CN)_4]^{--} \rightleftharpoons Cd^{++} + 4CN^-$$

and by the law of mass action (§ 110)

$$K = \frac{[Cd(CN)_4^{--}]}{[Cd^{++}]\,[CN^-]^4}.$$

K is the stability constant.

**172. Methods of Preparing Salts.**—The methods used to prepare salts are :—

(i.) The action of an acid upon a base.
(ii.) The action of an acid upon a metal.
(iii.) Double decomposition of an acid and a salt.
(iv.) Double decomposition of two salts.
(v.) Direct union of the elements concerned.

(i.) *Action of an Acid on a Base.*—Most soluble salts can be conveniently prepared by this method. If the base concerned is soluble, *i.e.*, an alkali, the acid is neutralised by it, the progress of the reaction being indicated by the use of litmus or some such indicator. Examples of such reactions are to be found in § 243.

This method is much used for preparing sodium and potassium salts.

If the base used is insoluble in water an excess of the base is added to the acid and the mixture is heated. When reaction has ceased the excess of base is filtered off and the filtrate evaporated and crystallised. This method is suitable for the preparation of the soluble salts of most of the metals. Either the oxide or hydroxide of the metal may be used ; the latter is always more readily attacked but is less commonly available, since many hydroxides are unstable.

(ii.) *The Action of an Acid on a Metal.*—If an acid reacts with a metal it usually gives a salt and hydrogen (but see §§ 126, 744). The method is often used on the commercial scale for preparing nitrates, chlorides and sulphates, but in the laboratory method (i) is found more convenient on account of the comparative slowness of the reaction between metals and acids as compared with the reactions of acids and bases.

(iii.) *Double Decomposition.*—Double decomposition taking place between an acid and a salt of a metal will yield the salt of the acid and metal if one of the products can be removed from the reaction mixture.

Thus sodium hydrogen sulphate can be made from sodium chloride and concentrated sulphuric acid,

$$NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl \uparrow,$$

because the hydrogen chloride passes off as a gas and equilibrium is not attained till all the reacting substances are transformed.

We can make sodium chloride from sodium hydrogen sulphate and hydrochloric acid if we add a large excess of concentrated hydrochloric acid to saturated sodium hydrogen sulphate solution. Sodium chloride is sparingly soluble in concentrated hydrochloric

acid (§§ 118, 249), and is precipitated and can be filtered off and dried.

$$NaHSO_4 + HCl \rightleftharpoons NaCl \downarrow + H_2SO_4.$$
$$Na^+ + Cl^- \rightleftharpoons [Na]^+ [Cl]^-.$$

It follows then that we can make the salt of a less volatile acid (sulphate, phosphate, etc.) by treating the salt of a more volatile acid (nitrate, acetate, carbonate, sulphide, etc.) with the less volatile acid.

A good many salts are made in this way from the *carbonates* of the metals. Thus calcium carbonate treated with nitric acid gives calcium nitrate, carbon dioxide and water.

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2 \uparrow.$$

Insoluble or sparingly soluble salts can also be made by the action of the acid on a soluble salt of the metal. Thus silver chloride is readily made by the action of hydrochloric acid on silver nitrate.

$$AgNO_3 + HCl = AgCl \downarrow + HNO_3.$$
$$Ag^+ + Cl^- \rightleftharpoons AgCl.$$

(iv.) *Double Decomposition of Two Salts.*—Any two salts when mixed in solution undergo double decomposition to some extent.

$$AB + CD \rightleftharpoons AD + CB.$$

Unless, however, one product is perceptibly less soluble than the other product and than the reacting salts, the method is not useful.

The method is greatly used for preparing insoluble salts. Thus on mixing a solution of a lead salt, say lead nitrate, and a sulphate, say sodium sulphate, insoluble lead sulphate is precipitated,

$$Pb(NO_3)_2 + Na_2SO_4 = PbSO_4 \downarrow + 2NaNO_3.$$

In actual fact the reaction takes place between the ions, and the equation is

$$Pb^{++} + 2NO_3^- + 2Na^+ + SO_4^{--} = PbSO_4 \downarrow + 2Na^+ + 2NO_3^-$$

which simplifies to

$$Pb^{++} + SO_4^{--} = PbSO_4 \downarrow.$$

The only chemical reaction which takes place is the combination of the lead ion and sulphate ion forming lead sulphate. This is instantly precipitated and the lead ion and sulphate ion continue to combine till only the very minute amount remains which is in

equilibrium with the small quantity of lead sulphate which can remain

$$Pb^{++} + SO_4^{--} \rightleftharpoons \underset{\text{Solution.}}{PbSO_4} \rightleftharpoons \underset{\text{Solid.}}{PbSO_4}$$

dissolved ($<0{\cdot}03$ gm. per litre).

The question of precipitation of insoluble salts is further discussed in § 119.

Occasionally a soluble salt is made by this method. Thus we may prepare copper formate by mixing equivalent quantities of solutions of copper sulphate and barium formate. The insoluble

$$CuSO_4 + Ba(H\,.\,COO)_2 = Cu(H\,.\,COO)_2 + BaSO_4\downarrow$$

barium sulphate is precipitated and may be filtered off, leaving copper formate in solution.

(v.) *Direct Union of the Elements.*—Direct union of the elements is often used in the preparation of chlorides and occasionally of bromides, iodides and sulphides.

Ferric chloride is prepared by passing chlorine over heated iron (§ 1170).

$$2Fe + 3Cl_2 = 2FeCl_3,$$

and mercuric sulphide by grinding mercury with sulphur,

$$Hg + S = HgS.$$

**173. General Properties of Salts.**—Salts are always solids at room temperature. Stannic chloride (§ 622) may, perhaps, be regarded as an exception, though in many respects it does not appear to be a true salt. They usually crystallise well, often with much water of crystallisation. Salts have, as a rule, high boiling points.

When dissolved in water solutions of salts are ionised and accordingly conduct electricity and manifest the various properties associated with ionisation and set out in § 116.

In their chemical reactions, like other electrovalent compounds, they readily undergo double decomposition. In consequence of their dissociation in solution their properties are largely additive.

**174. Additive Properties of Salts, also Acids and Bases.**—The properties of salts are in general *additive*. They have a set of properties corresponding to the acid radical and another set corresponding to the basic radical, and but few *constitutive* properties characteristic of the salt itself. This is very noticeable when the properties of solutions of salts are under consideration, for in dilute solution the undissociated salt is only present to a small extent, and in any case the reactions which characterise it are chiefly those of the ions. In the solid state this additive character is very

noticeable also, but applies more to chemical than to physical properties. Taking as an example, copper sulphate (p. 307) we find its properties falling into three groups :—

(1) A small group of properties characteristic of copper sulphate alone, *e.g.*, density, solubility and other physical properties, formation of hydrates, $CuSO_4 . 5H_2O$, etc.

(2) A group of properties characteristic of the cupric ion in general, *e.g.*,

Blue colour of solution. Poisonous properties.

Precipitates of insoluble copper compounds formed with ammonia, sodium carbonate, hydrogen sulphide, potassium ferrocyanide, etc.

Reduction to copper by strong reducing agents.

Reduction to cuprous oxide by glucose.

Liberation of iodine and precipitation of cuprous iodide when treated with potassium iodide.

Deposition of copper at the cathode on electrolysis.

(3) A group of properties characteristic of the sulphate ion. These include :

Decomposition to an oxide and sulphur trioxide when heated.

Precipitate given with barium and lead salts.

It is then possible to predict the properties of a salt from the properties of the acidic and basic radicals which compose it, and this fact makes it comparatively easy to acquire a knowledge of the properties of salts.

Suppose that twenty acids and forty metals are to be studied. These will form eight hundred salts. Owing to this additive character of their properties it is only necessary to know the sixty sets of properties corresponding to the acidic and metallic radicals and not the whole eight hundred sets of properties corresponding to the salts. In the later part of this book the characteristic properties of each set of salts are given under the respective acid or metal, while under the heading of the individual salt are given only its own specific properties, commercial uses, etc.

The possibility of a reasonably rapid qualitative analysis depends on this additive behaviour of salts. If we had to test separately for each of the very large number of salts the process of identifying a substance as a particular salt would be extremely lengthy. It is, however, only necessary to apply tests for the limited number of radicals or ions of which the salt may be composed.

**175. Basicity of Acids and Acidity of Bases.**—In §§ 159, 160 it was apparent that acids frequently contain more than one replaceable hydrogen atom in their molecule. The number of

replaceable hydrogen atoms in an acid is called its *basicity*, and acids are spoken of as monobasic, dibasic, etc. Thus we may give as examples :—

*Monobasic Acids.*—Hydrochloric acid HCl, nitric acid $HNO_3$, acetic acid $H \cdot C_2H_3O_2$.

*Dibasic Acids.*—Sulphuric acid $H_2SO_4$, carbonic acid $H_2CO_3$, oxalic acid $H_2C_2O_4$.

*Tribasic Acids.*—Phosphoric acid $H_3PO_4$, Orthoboric acid, $H_3BO_3$.

*Tetrabasic Acids.*—Orthosilicic acid $H_4SiO_4$. Few definite and stable tetrabasic acids, or acids of higher basicity, other than organic compounds, are known.

Bases may contain more than one hydroxyl group (– OH) per atom of metal or more than one oxygen atom per two atoms of metal. The number of hydrogen atoms with which one molecule of a base reacts when it reacts with an acid, is known as the acidity of a base. In the case of a hydroxide this number is equal to the number of hydroxyl groups in the molecule ; and in the case of an oxide to double the number of oxygen atoms in the molecule divided by the number of metalic atoms in the formula. As examples we may take :—

*Monacid Bases.*—Sodium hydroxide NaOH, cuprous oxide $Cu_2O$, (Ammonia $NH_3$).

*Di-acid Bases.*—Barium hydroxide $Ba(OH)_2$, lead oxide PbO.

*Tri-acid Bases.*—Aluminium hydroxide $Al(OH)_3$, ferric oxide $Fe_2O_3$.

*Tetracid Bases.*—Stannic hydroxide $Sn(OH)_4$, lead dioxide $PbO_2$

No true pentacid or hexacid bases are known. Thus uranium trioxide $UO_3$ does not form salts such as $UCl_6$, but rather $UO_2Cl_2$, only one of the oxygen atoms being replaceable. It is therefore a di-acid base.

**176. Equivalents of Acids and Bases.**—The *equivalents* of acids and bases are defined in the same manner as the equivalents of elements. The equivalent of an acid is the quantity by weight which will react with the equivalent of a metal. Now the equivalent of a metal (§ 34) is the quantity which will replace 1·008 parts by weight of hydrogen. *The equivalent of an acid is, therefore, the number of parts by weight of the acid which contains* 1·008 *parts by weight of replaceable hydrogen.*

The atomic weight of hydrogen is 1·008 ; thus the equivalent of an acid is its molecular weight divided by the number of replaceable hydrogen atoms contained in its molecule.

| Name of Acid. | Formula of | | Molecular Weight of Acid. | Equivalent. |
|---|---|---|---|---|
| | Acid. | Normal Sodium Salt. | | |
| Hydrochloric acid | $HCl$ | $NaCl$ | 36·46 | 36·46 |
| Sulphuric acid . | $H_2SO_4$ | $Na_2SO_4$ | 98 | 49 |
| Phosphoric acid . | $H_3PO_4$ | $Na_3PO_4$ | 98 | 32·67 |
| Acetic acid . | $C_2H_4O_2$ | $NaC_2H_3O_2$ | 60 | 60 |
| Tartaric acid . | $C_4H_6O_6$ | $Na_2C_4H_4O_6$ | 150 | 75 |

*The equivalent of a base is the number of parts by weight of it which reacts with* 1·008 *parts by weight of replaceable hydrogen forming a salt and water.*

One hydroxyl group reacts with one hydrogen atom,

$$NaOH + HCl = NaCl + H_2O$$
$$Ba(OH)_2 + 2HCl = BaCl_2 + 2H_2O,$$

and one oxygen atom reacts with two hydrogen atoms.

$$Ag_2O + 2HNO_3 = 2AgNO_3 + H_2O,$$
$$CuO + 2HCl = CuCl_2 + H_2O,$$
$$Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O.$$

It follows that the equivalent of a basic hydroxide is its molecular weight divided by the number of replaceable hydroxyl groups, and the equivalent of a basic oxide is its molecular weight divided by *twice* the number of replaceable oxygen atoms contained in its molecule.

| Name of Base. | Formula of | | Molecular Weight of Base. | Equivalent. |
|---|---|---|---|---|
| | Base. | Normal Salt. | | |
| Sodium oxide. . | $Na_2O$ | $NaCl$ | 62 | 31 |
| Sodium hydroxide . | $NaOH$ | $NaCl$ | 40 | 40 |
| Copper oxide . . | $CuO$ | $CuCl_2$ | 79·6 | 39·8 |
| Calcium hydroxide . | $Ca(OH)_2$ | $CaCl_2$ | 74 | 37 |
| Ferric oxide . . | $Fe_2O_3$ | $FeCl_3$ | 160 | 26·67 |
| Uranium trioxide . | $UO_3$ | $UO_2Cl_2$ | 285 | 142·5 |

One equivalent of any acid reacts with one equivalent of any base to form a normal salt. This fact is much used in volumetric analysis. The standard solutions in volumetric analysis are made up as a rule to a whole number of gram-equivalents or a simple sub-multiple or multiple of a gram-equivalent of the reagent per litre of solution.

A *normal solution* of a reagent contains one gram-equivalent per litre and, consequently, if two normal solutions react, equal volumes of each are required to complete the reaction.

A few examples of calculations based on the idea of equivalents are appended.

(1) *Twenty cubic centimetres of a solution containing* 24 *gms. of an acid per litre were neutralised by* 17 *c.c. of a solution of an alkali of strength* 0·75 *normal. Find the equivalent of the acid.*

A litre of the alkaline solution contained 0·75 gm.-equivalent.

$$\therefore \qquad 17 \text{ c.c. contained } \frac{0{\cdot}75 \times 17}{1{,}000} \text{ equivalents.}$$

This quantity reacted with 20 c.c. of acid solution.

$$\therefore \text{ 20 c.c. acid solution contains } \frac{0{\cdot}75 \times 17}{1{,}000} \text{ equivalents of acid.}$$

$$\therefore \text{ 1,000 c.c. acid solution contains } \frac{0{\cdot}75 \times 17 \times 1{,}000}{1{,}000 \times 20} \text{ equivalents.}$$

But this volume of acid solution contains 24 gms. of acid.

$$\therefore \qquad \frac{0{\cdot}75 \times 17}{20} \text{ equivalents} = 24{\cdot}0.$$

$$\therefore \qquad 1 \text{ equivalent} = \frac{24 \times 20}{17 \times 0{\cdot}75}$$

$$= 37{\cdot}65.$$

(2) *What weight of sulphuric acid will be enough to dissolve the copper oxide (CuO) formed by heating* 10 *gms. of copper in air ?*

One equivalent of copper produces one equivalent of copper oxide, which reacts with one equivalent of sulphuric acid. In CuO copper is bivalent. An

$$\text{equivalent of copper} = \frac{\text{atomic wt.}}{\text{valency}} = \frac{63{\cdot}6}{2}.$$

One equivalent of sulphuric acid $H_2SO_4$ is $\frac{98}{2}$.

$\therefore$ The oxide from $\frac{63{\cdot}6}{2}$ gms. Cu is neutralised by $\frac{98}{2}$ gms. $H_2SO_4$, and oxide from 10 gms. Cu is neutralised by $\frac{98 \times 10 \times 2}{2 \times 63{\cdot}6}$ gms. $H_2SO_4$.

$\therefore$ 15·41 gms. of sulphuric acid would react with the oxide produced from 10 gms. of copper.

# CHAPTER IX

## GROUP I. A.—HYDROGEN AND WATER

**177. Hydrogen and the Periodic Table.**—The element, hydrogen, is sometimes placed in the first group of the periodic table together with the alkali metals, lithium, sodium, potassium, rubidium and cæsium.

| *Group I. A.* | *Group I. B.* |
|---|---|
| (Hydrogen.) | |
| Lithium. | |
| Sodium. | |
| Potassium. | |
| | Copper. |
| Rubidium. | |
| | Silver. |
| Cæsium. | |
| | Gold. |
| (*Element* 87.) | |

The element hydrogen is, however, not necessarily classified with the alkali metals, for in the type of periodic table shown on pp. 158, 159, it could be placed at the head of any of the other groups without disturbing the regular sequence of atomic weights and atomic numbers (as indicated by atomic structure). The atomic structure of hydrogen is so far different from that of any other element that it does not fall naturally into any group of the periodic table. It is, however, more suitably classified with the alkali metals than with any other set of elements.

In the first place, hydrogen has a valency of one, which is the group-valency of the first and seventh groups, the alkali metals and the halogens. In its physical characteristics it resembles perhaps the latter group rather than the former, but the extreme lightness and smallness of its molecule as compared with those of other elements render comparisons of its physical properties of little value.

When dissolved in palladium (§ 1222) it seems to behave like a metal and form an alloy, rather than a compound of the usual type.

In chemical properties hydrogen resembles the alkali metals in the following respects :—

(1) It has a strong affinity for the non-metals and negligible

affinity for the metals. In this respect it differs completely from the halogens. Hydrogen is electropositive in character while the halogens are electronegative.

(2) Some of its compounds with non-metals and non-metallic groupings are electrolytes. These compounds are known as *acids* and are analogous in most respects to the *salts* formed by the union of metallic and non-metallic atoms and groupings. Thus HCl, hydrogen chloride, has, in a great number of its properties,[1] a strong resemblance to NaCl sodium chloride.

The analogy of hydrogen to the halogens rests on little else than their common univalent character. The fact that chlorine can replace hydrogen in such a compound as ethane $C_2H_6$, atom by atom forming such compounds as $C_2H_5Cl$, $C_2H_4Cl_2$, $C_2H_3Cl_3$, . . . $C_2Cl_6$ without producing any fundamental change in the character of these compounds has been adduced as evidence of a resemblance between hydrogen and the halogens. This argument is not without force, and it will be seen that the atomic structure of hydrogen bears a resemblance to that of both the alkali metals and the halogen.

The structure of the hydrogen atom is very simple (p. 170), for its atom consists only of a single outer electron and a nucleus consisting of a single proton. The alkali metal type is a nucleus, one or more complete "sets" of electrons and a single outer valency electron. The halogen type is a nucleus, one or more complete sets of electrons and an outer set of seven electrons.

The resemblance of the hydrogen atom to that of an alkali metal is clearer than its resemblance to that of a halogen.

Hydrogen can combine in two ways. If it forms hydrogen ion it loses its single outer electron. which is taken up by the acid radical. Thus the process of forming hydrogen bromide from hydrogen and bromine is the same as that

| Hydrogen bromide in solution. | | Sodium bromide. | |
|---|---|---|---|
| $\left[\begin{matrix}\text{Br}\\2\,.\,8\,.\,18\,.\,8\end{matrix}\right]^-$ | $\left[\begin{matrix}\text{H}\\\text{no electron}\end{matrix}\right]^+$ | $\left[\begin{matrix}\text{Br}\\2\,.\,8\,.\,18\,.\,8\end{matrix}\right]^-$ | $\left[\begin{matrix}\text{Na}\\2\,.\,8\,.\,-\,.\end{matrix}\right]^+$ |

of forming sodium bromide from sodium and bromine.

When, however, hydrogen forms a covalent compound, *e.g.*, $CH_4$ it shares electrons with the atom with which it combines (§ 154) so that in effect it *gains* an electron, and in this behaviour it is analogous to the halogens. In the hydrides of the alkali metals hydrogen forms a negative ion, strictly analogous to the negative ions of the halogens (§ 190).

Hydrogen, in fact, differs from all other elements in that by losing an electron it reaches a stable structure and by *gaining* an electron it also reaches a stable structure (He type). It has, therefore, analogies to both the first and seventh groups.

[1] Conductivity, behaviour on electrolysis, reaction with $AgNO_3$, $Pb(NO_3)_2$ etc.

**178. Discovery of Hydrogen.**—The first mention of a gas evolved by the action of acids on metals was made by Paracelsus in the sixteenth century. The gas produced in this way was later known as "inflammable air," but was confused at first with carbon monoxide, hydrogen sulphide, etc. Henry Cavendish, in 1766, was the first to describe its properties and characterise it as a definite substance. The gas was also known as phlogisticated air and even identified with phlogiston itself, the imaginary principle of combustibility (§ 9). In 1783 the name hydrogen was given to the gas by Lavoisier.

Cavendish, in 1781, proved conclusively that water was the only product of the combustion of hydrogen and oxygen, a matter further discussed in § 196.

**179. Occurrence.**—Hydrogen occurs in the gases evolved from certain volcanoes, and is said to form about one hundred-thousandth part of the lower atmosphere. Hydrogen also exists in the free state in the atmosphere of the sun.

Combined hydrogen exists in enormous quantity in water, of which it forms one-ninth part by weight, and in smaller quantities

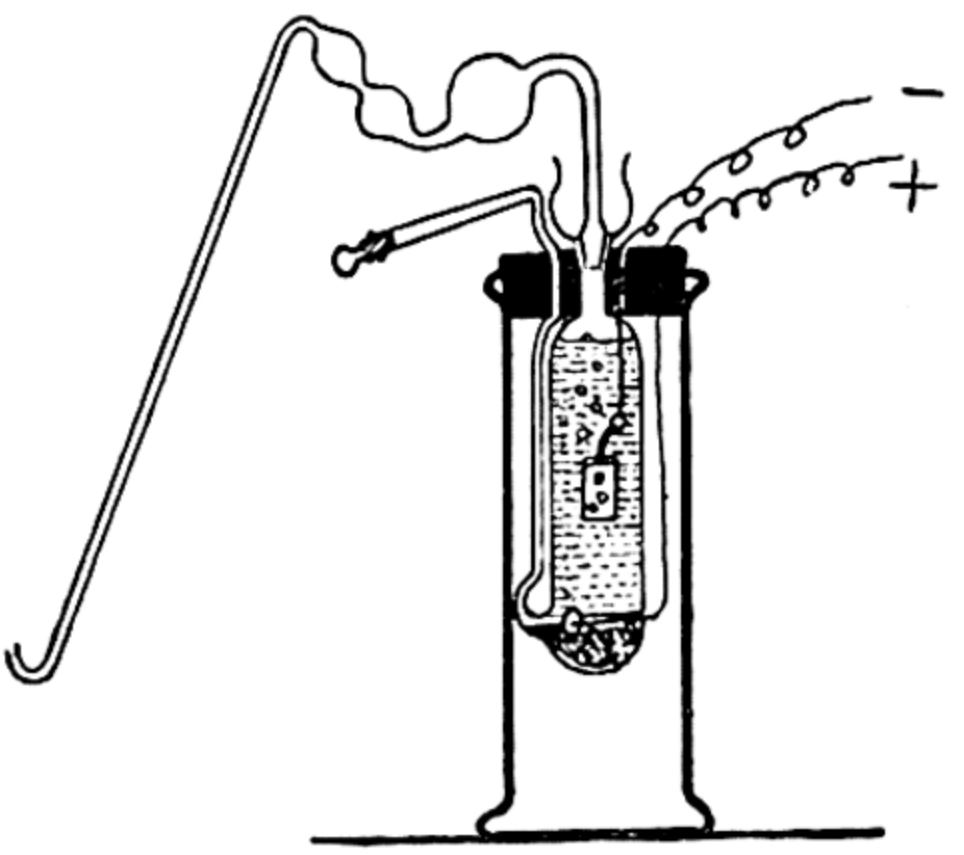



FIG. 61.—Bunsen Voltameter.

in naturally-occurring petroleum, coal, methane, hydrogen sulphide, etc. Almost all organic compounds contain a proportion of hydrogen, varying from 25 per cent. to 1 per cent. or even less.

**180. Preparation and Manufacture of Hydrogen.**—The methods used to prepare hydrogen are of three main tyes :—

(1) The electrolysis of solutions.

(2) The displacement of hydrogen from its compounds by reaction with a more electropositive element.

(3) Thermal decomposition of compounds containing hydrogen.

**181. Preparation of Hydrogen by Electrolysis.**—Pure water cannot be electrolysed, for it is so slightly ionised that it is almost a non-

conductor. It is, however, possible to electrolyse water in presence of certain acids, bases or salts and in general, *the electrolysis of solutions of acids and of compounds of the more electropositive metals* (*e.g.*, *the alkali metals, alkaline-earth metals and magnesium*) *will yield hydrogen*.

(1) *Electrolysis of Dilute Sulphuric Acid.*—This method of preparing hydrogen is slow, for we know that to obtain one equivalent of hydrogen (11·2 litres at N.T.P.) we require 96,494 coulombs of electricity, *i.e.*, a current of about 2·25 amperes continuing for twelve hours. The forms of laboratory apparatus used for the demonstration of the electrolysis of water have a comparatively high resistance due to the small size of the electrodes and their distance apart and consequently it is difficult to make more than some 50 c.c. of hydrogen per hour in this way. The Bunsen voltameter (Fig. 61) gives a better supply of pure hydrogen. The electrode at which the hydrogen is to be evolved is of platinum, but the oxygen electrode is of zinc amalgam with which the sulphate group combines as soon as formed, and consequently, no oxygen is evolved.

Sulphuric acid dissociates.

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}.$$

The attraction of the charged anode and cathode causes these ions to wander to them.

At the cathode

$$H^+ + \ominus = H$$
$$H + H = H_2 \uparrow$$

At the anode $SO_4$— ion accumulates but, being very stable, is not discharged.

The metal of the anode (unless it is of gold or platinum) loses electrons becoming an ion,

$$Zn = Zn^{++} + 2\ominus$$

Thus in the Bunsen voltameter zinc ions and sulphate ions accumulate round the cathode.

The gas obtained in this way may contain traces of volatile impurities, especially arsine $AsH_3$, derived from the action of the hydrogen on traces of arsenic often present in sulphuric acid.

Hydrogen has been made on the commercial scale by the electrolysis of dilute acid, using large lead electrodes, but the process has not proved very successful.

(2) *Electrolysis of Alkalis.*—Very pure hydrogen is obtained by

electrolysing alkalis. Barium hydroxide $Ba(OH)_2$ is used, since its solutions are always free from carbonates (§ 394).

The method was employed by Noyes for making the hydrogen for his very accurate determination of the atomic weight of hydrogen, and is further described on p. 75.

The reactions are :—

$$Ba(OH)_2 \rightleftharpoons Ba^{++} + 2OH^-$$

At the cathode barium ion $Ba^{++}$ accumulates and hydrion derived from the water is discharged, its place being supplied by fresh dissociation of the water.

$$2H^+ + 2\ominus = H_2$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

At the anode
$$2OH^- = 2OH + 2\ominus$$
$$2OH = H_2O + O$$
$$O + O = O_2.$$

Since barium ion is not discharged and an $OH^-$ group is set free from the water for every one discharged at the anode, the only substance used up is water and the net result is

$$2H_2O = 2H_2 + O_2.$$

The gas obtained in this way is almost pure but not dry. Hydrogen is best dried by passing it over anhydrous calcium chloride, followed by phosphorus pentoxide, for the gas reduces sulphuric acid to a very slight extent, forming sulphur dioxide. Hydrogen has also been purified by freezing out all impurities with liquid air, for with the exception of helium, neon and hydrogen all gases condense to liquids at the low temperature of boiling liquid air.

(3) *Commercial Preparation of Hydrogen by Electrolysis.*—Sodium chloride solution is electrolysed on the large scale in the manufacture of caustic soda [§ 230 (2)]. Sodium is liberated and reacts with the water present, giving caustic soda and hydrogen.

$$2Na + 2H_2O = 2NaOH + H_2.$$

This process furnishes most of the hydrogen sold.

**182. Preparation of Hydrogen by Displacement from Water.**—*The Action of Metals on Water.*—Water is decomposed in the cold by the alkali metals, by calcium, strontium, barium, and less readily by thallium and magnesium and by the aluminium-mercury couple.

(1) *Action of Metals on Cold Water.*—Sodium may be used in the laboratory to make hydrogen. Its action on water is very vigorous

and may be exceedingly dangerous (see § 224), and is therefore hardly a practical method. The action of steam on sodium has been used to furnish very pure hydrogen.

$$2H_2O + 2Na = 2NaOH + H_2.$$

If it is desired to collect hydrogen from the reaction of sodium and water, the metal, in pieces not larger than a pea, may be held under water with a wire gauze spoon (Fig. 62), or pressed into a lead tube and immersed beneath an inverted jar of water. Alloys of lead and sodium have been used and also sodium amalgam (§ 437). These alloys react with water without undue violence. The action of potassium on water is inconveniently violent. Calcium sinks beneath the water and decomposes it steadily, especially if warm. The gas produced is usually impure, since commercial calcium contains traces of carbide.

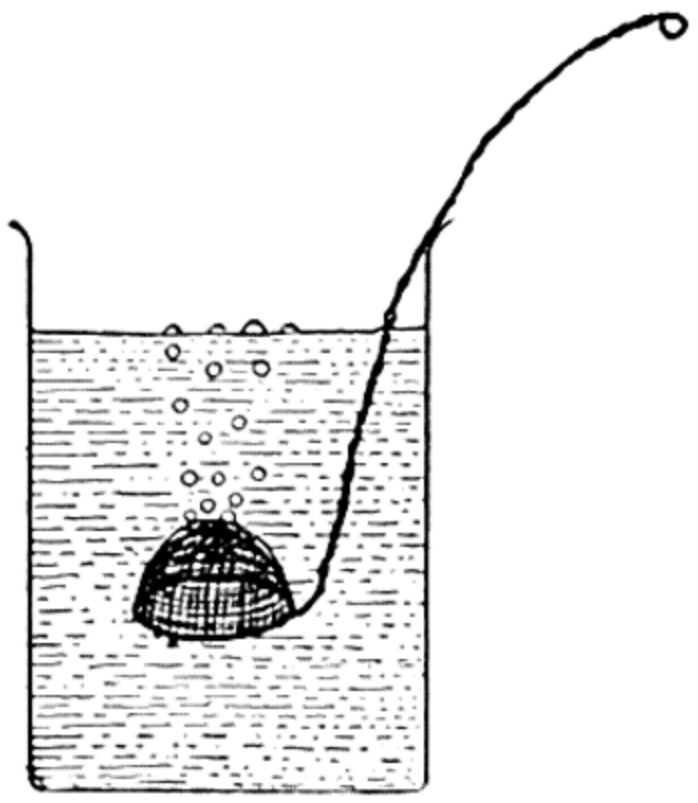


FIG. 62.—Reaction of sodium with water.

(2) *Action of Heated Metals upon Steam.*—The action of certain heated metals on steam yields the oxides of the former together with hydrogen. The platinum metals (except osmium), gold, silver and mercury, are not affected under any conditions; copper and lead react only at a white heat. The other metals react with steam at a red heat or below, and, of these, zinc, iron and magnesium are most suitable. The action of iron is still used commercially where electrolytic hydrogen is not available. Steam is passed over red-hot iron, yielding triferric tetroxide and hydrogen,

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2.$$

The iron oxide is then re-converted into metallic iron by passing over it water-gas (§ 556) a mixture of hydrogen and carbon monoxide,

$$Fe_3O_4 + 4H_2 \rightleftharpoons 3Fe + 4H_2O$$
$$Fe_3O_4 + 4CO \rightleftharpoons 3Fe + 4CO_2.$$

The iron so obtained is then again treated with steam. In this way hydrogen is made without expenditure of iron, the only substance actually used up being the coke employed in making the water-gas.

Magnesium burns brightly in steam, forming its oxide and hydrogen,

$$Mg + H_2O = MgO + H_2$$

(3) *Commercial preparation of hydrogen from water-gas* (§ 556):

When steam is passed over red-hot, or better, white-hot coke the reaction

$$C + H_2O = CO + H_2 - 29 \text{ Cals.}$$

takes place, carbon monoxide and hydrogen being formed. Since heat is absorbed when the reaction takes place, the coke soon becomes too cool to react. When this occurs it is re-heated by blowing air through it until it is once more hot enough to react with steam. Alternate subjection to a blast of air (the issuing gases being allowed to escape) and to a blast of steam (the issuing gases being collected) results in the production of *water-gas* containing about

| | |
|---|---|
| Hydrogen | 50 per cent. |
| Carbon monoxide | 43 „ |
| Carbon dioxide | 4 „ |
| Nitrogen | 2 „ |
| Other gases | 1 „ |

The separation of reasonably pure hydrogen from the mixture is carried on by two chief methods.

(*a*) *The Iron Process.*—In this process a mixture of water-gas and steam is passed over certain catalysts, notably nickel, iron or chromium salts, when the reaction to hydrogen and carbon dioxide takes place.

$$H_2 + CO + H_2O = 2H_2 + CO_2.$$

The gases under pressure are passed through water, in which carbon dioxide dissolves, while hydrogen, which has only about a hundredth of its solubility, passes on.

(*b*) The Linde-Caro process depends on the fact that hydrogen boils about 80° C. lower than carbon monoxide and that it is possible to liquefy the carbon monoxide by regenerative cooling (cf. p. 501) leaving hydrogen as a gas. The gas has to be cooled beforehand by liquid air owing to the positive Joule-Thomson effect of hydrogen. The method is used to a less extent than the iron process.

**183. Preparation of Hydrogen by Displacement from Acids.**—Solutions of acids contain hydrion, $H^+$, which reacts with certain metals giving the metallic ion and hydrogen. Very weak acids react with metals very slowly on account of the small amount of hydrion they produce, and acids which are oxidising agents (*e.g.*, nitric and chromic acids) react with the hydrogen formed. Dilute hydrochloric and sulphuric acids, being strong and not able to react with hydrogen are the most suitable. The metals which are less electropositive than hydrogen do not displace it from hydrion, and so copper, mercury and the noble metals are not available. Others, such as lead, react very slowly; and such metals as magnesium,

zinc, and iron are most suitable. Magnesium yields a very pure gas, but is little used on account of its expense.

(1) *Action of Iron upon Acids.*—The action of dilute acids upon commercial iron (which always contains carbides, silicides, etc.) yields a highly impure gas, containing hydrides of carbon, hydrogen silicide, phosphine, hydrogen sulphide, etc. It is not used, therefore, as a source of hydrogen in the laboratory, although in the past the action of acids on scrap iron was of use as a large-scale method for making hydrogen for filling balloons,

$$Fe + 2H^+ = Fe^{++} + H_2$$

*or*

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

(2) *Action of Zinc on Acids.*—The action of zinc upon dilute hydrochloric or sulphuric acid is ordinarily used to make hydrogen. The action proceeds smoothly without heating, and Kipp's apparatus may therefore be used to ensure a supply of hydrogen whenever required. If the hydrogen is required under some pressure (as for filling rubber balloons) a stout glass bottle, fitted with a delivery tube and a tap funnel, may be used. If the metal and acid used are very pure, very pure hydrogen is obtained, but the action is very slow. Commercial zinc and dilute sulphuric acid (1 : 8) or hydrochloric acid (1 : 2) evolve a brisk stream of gas, the very soluble zinc chloride or sulphate,

$$Zn + 2H^+ = Zn^{++} + H_2$$

*or*

$$Zn + 2HCl = ZnCl_2 + H_2$$
$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

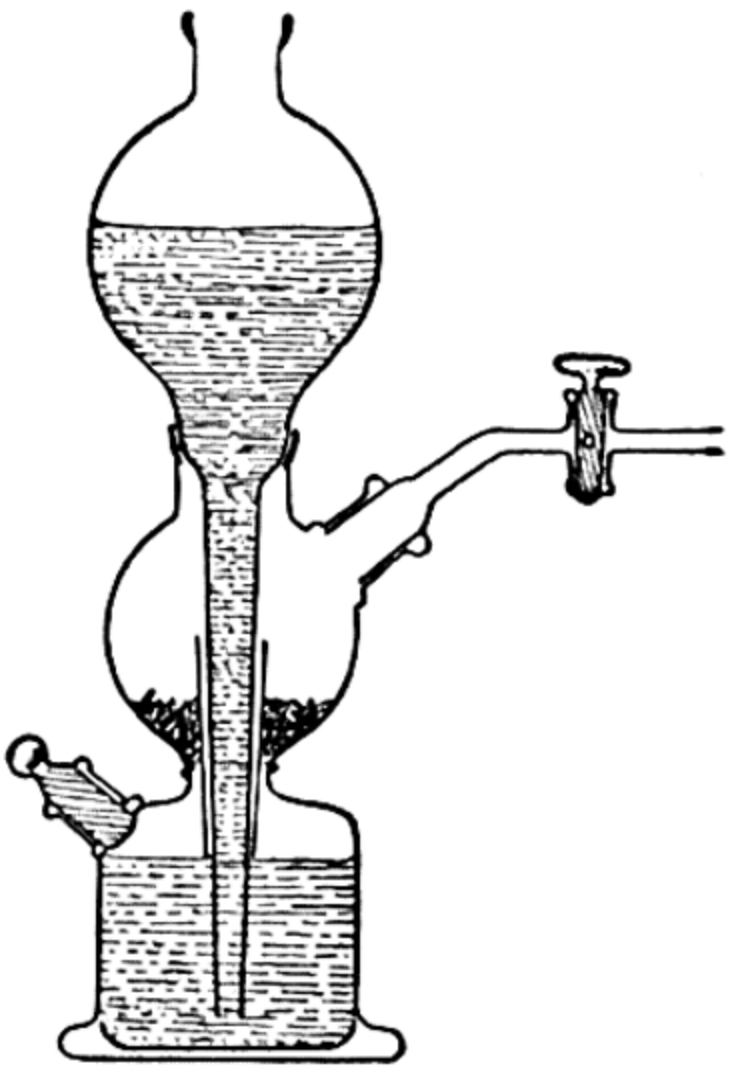


FIG. 64. — Preparation of hydrogen from zinc and dilute acid.

being left in solution. The gas so obtained may contain, beside water vapour, traces of the hydrides of sulphur ($H_2S$), arsenic ($AsH_3$), antimony ($SbH_3$), carbon ($C_2H_2$, etc.), silicon ($SiH_4$), phosphorus ($PH_3$), and often traces of oxides of carbon, originally occluded by the zinc. These impurities, though numerous, form only a minute proportion of the gas. The best method of purifying the gas is washing it (1) with strong potassium permanganate solution, which oxidises most of the hydrides, and then (2) with silver nitrate solution, which removes the last traces of arsine, etc. The gas is

then dried, first with calcium chloride, then with phosphorus pentoxide.

Hydrogen may be collected over water or mercury, or if not required very pure, by upward displacement.

**184. Hydrogen by Displacement from Alkalis.**—Most elements which form oxyacids dissolve in alkalis and either form a hydride or produce hydrogen (*v.* p. 265). Hydrogen may be produced by the action of alkalis on zinc, aluminium, tin and silicon.

Each of these elements, when heated with warm concentrated caustic soda, evolves hydrogen. The purity of the latter depends on the purity of the metal. Aluminium produces a very pure gas. Sodium zincate, aluminate, stannite or silicate are produced together with hydrogen.

(*a*) $$Zn + 2NaOH = Na_2ZnO_2 + H_2$$

(*b*) $$2\,Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2$$

(*c*) $$Sn + 2NaOH = Na_2SnO_2 + H_2$$

(*d*) $$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2.$$

The rate of the reaction of zinc and caustic soda is very much less than that of zinc and dilute sulphuric acid, and the method is not used for the preparation of the gas in any quantity.

Hydrogen has been prepared for balloons by igniting a mixture of ferrosilicon (90–95 per cent. Si), caustic soda and lime in a "cartridge" from which air is excluded. The mixture affords a portable means of preparing hydrogen under military conditions. The reaction is that of equation (*d*) above.

**185. Hydrogen from Hydrides and other Hydrogen Compounds.**—(1) *Calcium hydride*, $CaH_2$, reacts with water, one gram giving more than a litre of gas,

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2.$$

It is known as hydrolith and has been employed as a convenient and portable means of preparing hydrogen for small balloons. It is too expensive for large-scale use except in warlike operations where expense is no object. It is also sold in cubes for laboratory use.

(2) *Decomposition of Hydrogen Compounds by Heat.*—Hydrogen may also be made by the action of heat on sodium formate, sodium oxalate being left behind:

$$\begin{matrix} NaO\,.\,OCH \\ NaO\,.\,OCH \end{matrix} = \begin{matrix} NaO\,.\,OC \\ | \\ NaO\,.\,OC \end{matrix} + H_2.$$

(3) The action of heat on certain unstable hydrides, *e.g.*, copper hydride yields hydrogen.

The methods are not practically important.

**185a. Industrial Preparation of Hydrogen.**—The two most important methods are by separation from water-gas as indicated in § 182, but the following are also of industrial importance :—

(1) The electrolysis of aqueous sodium chloride in the manufacture of NaOH (§ 230).

(2) The thermal decomposition or ' cracking ' of hydrocarbons, such as natural gas.

(3) The cracking of ammonia.

**186. Forms of Hydrogen.**—A few years ago it was theoretically proved that two varieties of hydrogen must exist, one of which, *ortho-hydrogen*, has the nuclei of the two atoms of its molecule rotating in the same sense, while the other, *para-hydrogen*, has nuclei rotating in opposite senses. The two forms were duly discovered. They differ in certain physical properties, *e.g.*, specific heat, but are identical in chemical behaviour. Hydrogen at ordinary temperatures contains about three parts of ortho-hydrogen to one of para-hydrogen. Deuterium and atomic hydrogen are discussed in §§ 193a, 193.

**187. Atomic Weight and Formula.**—The atomic weight of hydrogen and its formula are discussed in the chapter on atomic weights (§§ 48, 49, 69).

**188. Properties of Hydrogen.**—Hydrogen is a colourless gas which when pure has neither taste nor smell. As ordinarily made it contains traces of hydrocarbons which give it an unpleasant acetylene-like odour. The gas is non-poisonous but does not support life. The gas as prepared from cast-iron, etc., contains arsine $AsH_3$, and is seriously poisonous. Danger may thus be caused to the health of workers engaged in cleaning castings with acid (' pickling '). Hydrogen has a lower density than any other gas. Its density, relative to oxygen as 16·000, is 1·008. Relative to air its density is 0·069, and relative to water, 0·0000899 at N.T.P.

Hydrogen is liquefied only with great difficulty. The principle of regenerative cooling (cf. p. 501) can only be employed at temperatures below – 205° C., for above that temperature the Joule-Thomson effect is positive, *i.e.*, heat is not absorbed but, on the contrary, produced when hydrogen is allowed to expand without doing work. At very low temperatures the Joule-Thomson effect becomes negative, and thus hydrogen can be liquefied by the usual forms of apparatus if it is previously cooled to – 205° C.

Liquid hydrogen boils at – 252·5° and solidifies at – 257°. It was at one time thought that solid hydrogen would be metallic in character, from its analogy to the alkali metals, but this is not the case. Liquid hydrogen is lighter than any other solid or liquid, its density being 0·07.

Hydrogen is very sparingly soluble in water, 100 volumes of which dissolve about 2 volumes of the gas at 0° C. and less at higher temperatures.

The visible spectrum of hydrogen is more simple than that of most elements. It contains a series of prominent lines interspersed with fine lines. Balmer, in 1885, showed that the frequency of the light of these lines was given (with an accuracy of 1 part per million) by the formula $R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$, where R is a constant and $n$ a small whole number 3, 4, 5, etc. The quantum theory of spectra accounts for this remarkable fact, and by making allowance for the alteration of mass of the electrons with velocity according to principles of relativity the whole fine line spectrum appears to be accurately accounted for.

**189. Reactions with Non-metallic Elements.**—Hydrogen burns in air or oxygen with a hot and almost colourless flame. The flame is yellow when burned from a glass jet, owing to volatilisation of sodium compounds. The product is water,

$$2H_2 + O_2 = 2H_2O,$$

and minute traces of hydrogen peroxide also are found.

Hydrogen and oxygen react immeasurably slowly at room temperature, perceptibly at 180° C., and with explosion at 550° C. It is said that pure intensively-dried gases (§ 205) do not combine even at 900° C.

In presence of certain catalysts, notably platinum black and palladium black, union takes place at room temperature, so much heat being evolved that the gas ignites. The phenomenon is further discussed under platinum (§ 1229).

Hydrogen and fluorine combine instantly, even in the dark, with explosion,

$$H_2 + F_2 = H_2F_2.$$

Hydrogen combines directly with chlorine at ordinary temperatures if the mixed gases are exposed to light, or if they are heated to *c.* 400° C. Hydrogen chloride is formed.

$$H_2 + Cl_2 = 2HCl.$$

Bromine and hydrogen combine above 400° C., giving hydrogen bromide,

$$H_2 + Br_2 = 2HBr.$$

The reaction proceeds rapidly in presence of platinum as a catalyst.

Hydrogen and iodine vapour combine reversibly at temperature above 400° C.

$$H_2 + I_2 \rightleftharpoons 2HI.$$

Sri Pratap College,

The reaction is very slow, but is enormously accelerated in presence of platinum black.

Hydrogen also combines directly with sulphur, selenium, and tellurium at temperatures from 250–400° C., the hydrides $H_2S_3$, $H_2Se$, $H_2Te$ being formed reversibly, though only in small proportion.

$$H_2 + S \rightleftharpoons H_2S.$$

With nitrogen at 200° C. upwards ammonia is formed by the reversible reaction,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3.$$

The proportion of ammonia produced is small, but is much increased by increase of pressure. The reaction is very slow unless accelerated by the use of suitable catalysts. The rate of formation of ammonia at atmospheric pressure is almost negligible (§ 689).

Hydrogen combines directly with carbon at about 1,150° C., forming small amounts of methane $CH_4$. When an arc is struck between carbon poles in an atmosphere of hydrogen, some acetylene $C_2H_2$ is formed.

**190. Reactions with Metals.**—Hydrogen in general does not react with the metals. Somewhat unstable compounds are, however, formed with the alkali metals, alkaline-earth metals and the rare-earths. Examples are NaH sodium hydride, $CaH_2$ calcium hydride and $LaH_3$ lanthanum hydride.

These hydrides, unlike all others, are ionised salt-like compounds, and have been shown to contain *negative* hydrogen ions $H^-$. Thus the formula of sodium hydride may be written $Na^+ [H^-]$. Hydrogen can either lose an electron and form the ordinary hydrogen ion $H^+$, or, in these compounds only, gain an electron and so form an ion of the helium pattern. This is one respect in which it resembles the halogens.

Hydrogen is absorbed by certain metals, such as palladium, platinum, nickel, etc. The table below shows the volume of gas taken up by 1 volume of the metal :—

| Element. | Number of Volumes of Hydrogen occluded. |
|---|---|
| Iron (reduced powder) . . . . | 0·4–19·2 |
| Cobalt . . . . . | 59–193 |
| Platinum (spongy) . . . . | 110 |
| Palladium . . . . . | 850 |

It seems almost certain that this gas is not chemically combined. It is more active than ordinary hydrogen, but this may be due to

the electrical effect resulting from the voltaic couple, consisting of hydrogen and a metal such as platinum, to which it is strongly electropositive. The effect may also be due to the high concentration of hydrogen present, for a consideration of the volume of hydrogen in a given space makes it clear that adsorbed hydrogen is equivalent to hydrogen compressed to the enormous extent of 50–850 atm. Numerous reactions between hydrogen and compounds of various types take place easily if a mixture of hydrogen and the vapour of the substance is passed over a finely divided metal, usually platinum or nickel (see also § 1202).

**191. Reaction with Compounds.**—Hydrogen reacts with very few compounds in the cold and at atmospheric pressure. It will, however, displace the noble metals from their salts ; itself behaving like a metal in this respect,

$$2AgNO_3 + H_2 = 2Ag + 2HNO_3.$$

Hydrogen under pressure is more effective.

The oxides of such metals as are not markedly more electropositive than hydrogen are reduced by hydrogen at temperatures varying from c. 100° C. (silver oxide) upwards. Thus copper oxide begins to be reduced at 90° C. and is quickly acted on at 200° C.

$$CuO + H_2 = Cu + H_2O.$$

Ferric oxide is reduced first to lower oxides at about 220° C. and finally to metal at a little over 300° C.

$$3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O$$
$$Fe_3O_4 + H_2 = 3FeO + H_2O$$
$$FeO + H_2 = Fe + H_2O.$$

The oxides of the alkali metals, the alkaline earths, zinc and aluminium are not reduced by hydrogen.

Many chlorides are reduced when heated in a current of hydrogen. Thus silver chloride yields the metal and hydrogen chloride,

$$2AgCl + H_2 = 2Ag + 2HCl.$$

**192. Nascent Hydrogen.**—While hydrogen is not at ordinary temperatures a particularly active gas, hydrogen at the moment of its liberation by a chemical reaction or by electrolysis shows greater chemical activity. This hydrogen at the moment of formation is said to be *nascent*. Hydrogen absorbed by metals has also something of the same activity.

Thus chlorates are reduced to chlorides and ferric salts to ferrous salts when hydrogen is generated in their solutions, but not when hydrogen is merely passed through them,

$$KClO_3 + 6H = KCl + 3H_2O$$
$$FeCl_3 + H = FeCl_2 + HCl.$$

It was at one time believed that this superior activity of nascent hydrogen was due to the fact that in gaseous hydrogen the atoms (H) are combined into molecules ($H_2$). Consequently, work has to be done in converting these molecules of gaseous hydrogen into atoms before chemical reaction can take place. Nascent hydrogen is, however, presumably liberated in the form of atoms, and these need no work done on them, but are at once ready to react. This attractive theory, however, does not explain the fact that all nascent hydrogen is not equally reactive. Actually, nascent hydrogen evolved from zinc and sulphuric acid will reduce chlorates to chlorides, while the nascent hydrogen from sodium amalgam has no effect. Similar differences are found in the reducing action of hydrogen liberated by electrolysis at cathodes of different metals. Thus hydrogen liberated at a lead plate is much more effective than hydrogen liberated at a silver plate.

The theory of the superior activity of nascent hydrogen being due to its consisting of single atoms is probably untrue, and the differences between the nascent hydrogen evolved in different reactions is probably due to the different chemical energy of the reactions. The whole of the energy liberated in the reaction producing the hydrogen does not appear as heat, but a part of it increases the chemical energy of the hydrogen molecule as liberated. This would account for the variation in its activity. In the case of electrolytic hydrogen, it is found that the metals at which is produced the most reactive hydrogen are those which require the highest voltage to produce it at all. The hydrogen produced at higher voltages perhaps carries with it some of the extra electrical energy, which enhances its chemical activity. Thus, to electrolyse dilute sulphuric acid with a lead cathode, 0·49 volts are required in excess of the voltage needed with a silver cathode, and in general the reducing power and 'over-voltage' run parallel.

Convenient sources of 'nascent hydrogen' are a mixture of a metal and acid, sodium amalgam in contact with water, a metal 'couple,' such as the aluminium-mercury couple, or the cathode of an electrolytic cell where hydrogen is being evolved. The last method is known as electrolytic reduction and is convenient where time is not an object. It has the advantage that no metallic compound has to be mixed with the substance to be reduced, and the degree of reduction obtainable is also very considerable. The process is, moreover, easily controlled, the degree of reduction depending on the current density, nature of the cathode, etc.

**193. Atomic Hydrogen.**—The hydrogen molecule is dissociated into single atoms at very high temperatures and also by the action of the electrical discharge. Hydrogen, at a pressure of less than half a millimetre of mercury, when subjected to an electrical discharge, is almost completely decomposed into single atoms, $H_2 = 2H$. These recombine almost instantaneously unless all glass surfaces with which they are in contact are scrupulously cleansed from catalysts. This atomic hydrogen is very reactive. It reacts with sulphur and phosphorus, and even some metals, in the cold, forming their hydrides, and reduces cupric and ferric oxides in the cold.

**193a. Deuterium, Heavy Hydrogen.**—Isotopes (§150) of an element have identical nuclear charges but different atomic masses. The normal hydrogen atom has a nucleus of mass 1 and charge 1 with one electron rotating round it. Its simplest isotope would have a nucleus of mass 2, charge 1, with one electron rotating round it. The discovery of the hydrogen isotope was due to a discrepancy between the very exact physical and chemical atomic weights of hydrogen. The mass-spectrograph indicated a mass of 1·0078 for hydrogen taking the isotope $O^{16} = 16{\cdot}0000$ as standard. Chemical methods also gave the same value 1·0078 taking ordinary oxygen, $O^{16}$ with a minute proportion of $O^{17}$ and $O^{18}$, as standard = 16·0000. Thus the chemical value—the average for all H isotopes present—is higher than the physical value, which was the atomic weight of $H^1$ only.

Evidence for the existence of an $H^2$ isotope was sought. Washburn, Urey and others showed that heavier fractions could be separated from hydrogen and its compounds, and these have since been found to contain about one part in 5,550 of the isotope of mass 2. This was named *deuterium* and is given the symbol D. A separate symbol is employed for this isotope because its compounds can be studied. Other isotopes cannot be separated to a sufficient extent to allow of this, nor do the compounds of the several isotopes of other elements than hydrogen differ to a detectable extent.

Since the deuterium atom is twice as heavy as that of hydrogen (A.W. 2·0137), it and its compounds are denser and this is the chief means of detecting a separation.

*Separation of Deuterium and "Heavy Water."*—Numerous methods are possible but only (2) below is of practical value. Water rich in deuterium has been separated by several methods, of which the chief are :

(1) Fractional Distillation of Water. "Heavy water" ($D_2O$ and HDO) is less volatile than water $H_2(O)$.

(2) Electrolysis of Water. This method, employed by G. N. Lewis, who was the first to separate pure heavy water, has proved the most valuable. When a solution of alkali is electrolysed, the hydrogen given off contains only about one-fifth of the proportion of deuterium

contained in the original water. By starting with 20 litres of water, already somewhat enriched by electrolysis and continuing electrolysis until only 1·5 c.c. remained, fairly pure "heavy water" containing 66 per cent. $D_2O$ was obtained by Lewis, and by combining the products of several electrolyses about 1·3 c.c. of almost pure $D_2O$ resulted.

From this product deuterium $D_2$ was prepared and obtained in a pure state by diffusion.

"Heavy water," $D_2O$, differs in physical properties from $H_2O$. Thus we have :—

| | $D_2O$ | $H_2O$ |
|---|---|---|
| M.P. . . . . | 3·8° C. | 0° C. |
| B.P. . . . . | 101·42° C. | 100° C. |
| S.G./20° C. . . . . | 1·1071 | 1·0 |
| Temperature of maximum density . . . . | 11·6° C. | 4° C. |
| Viscosity (centipoises) . . | 12·6 | 10·87 |
| Specific heat . . . | 1·018 | 1·000 |
| Refractive index $n_D^{20}$ . . | 1·3281 | 1·3329 |

In addition to the above properties, certain solubilities (NaCl, $BaCl_2$) have been found to be less in $D_2O$ than in $H_2O$ by about 15 per cent. The mobility of ions in $D_2O$ is less than that in $H_2O$.

The chemical differences are on the whole very slight. The reaction velocity in general appears to be smaller. Among the most interesting pieces of knowledge obtained by the use of heavy hydrogen is the ready exchange between hydrogen atoms.

If ammonium chloride is dissolved in heavy water, the same proportion of deuterium is found in the salt recovered by evaporation as in the water used. Clearly there must be an interchange of hydrogen atoms between $NH_4^+$ and $H_2O$ or $D_2O$, perhaps

$$NH_4^+ + OD^- \rightleftharpoons NH_4OD \rightleftharpoons NH_3D^+ + OH^-.$$

Again, when hypophosphorous acid $H_3PO_2$ is dissolved in heavy water it is converted into $DH_2PO_2$—evidence that only one of the hydrogen atoms in hypophosphorous acid is ionisable (§ 777).

Mixed molecules such as HD, DOH, etc., are readily formed. Thus a mixture of light and heavy water is in chemical equilibrium.

$$D_2O + H_2O \rightleftharpoons 2DOH.$$

Heavy water is now available in large quantities and is likely to be of use in the liberation of atomic energy.

**194. Uses of Hydrogen.**—Hydrogen finds its chief use in the manufacture of ammonia (§ 689) and in the hydrogenation of oils (§ 1202). The use of hydrogen in the preparation of synthetic methyl alcohol and also synthetic petrol, is becoming increasingly

important. Quantities are also used for filling balloons (*v.* also under Helium, § 1245).

The lifting force of the gas in a balloon is equal to the difference of weight between the volume of air displaced by it and the weight of the envelope and the contained gas. A litre of hydrogen at, say, 15° C. will lift the weight of a litre of air at that temperature less the weight of the litre of hydrogen. A litre of hydrogen will, therefore, lift

$$\left(\frac{14{\cdot}4 - 1}{11{\cdot}2}\right)\frac{273}{288} = 1{\cdot}13 \text{ gms.}$$

The oxyhydrogen blow-pipe has been largely replaced by the oxy-acetylene instrument (§ 865) but the air-hydrogen blow-pipe flame is still used in the autogenous soldering of lead. Leaden vessels for holding acids, lead chambers for the sulphuric acid process, etc., cannot be soldered in the ordinary way, for there would be rapid corrosion at the point where the solder and lead met. They are therefore *autogenously* welded by melting the edges together. The hydrogen-air flame is clean, hot and reducing in character and, therefore, very suitable for the purpose. The hydrogen is usually generated in a piece of apparatus like a large "Kipp."

**195. Detection and Estimation.**—Combined hydrogen is best detected by heating the compound suspected of containing it with copper oxide, which in most cases oxidises the hydrogen to water, which may be condensed and identified by the tests mentioned on p. 249. The water may by suitable methods be absorbed in weighed drying vessels and its weight determined. These processes are chiefly of use in organic chemistry and are described in text-books dealing with that subject.

Free hydrogen may be identified by its burning with a nearly colourless flame (quite different in appearance from those of carbon monoxide, hydrogen sulphide, etc.), yielding a residual gas free from carbon dioxide. Small quantities of hydrogen, mixed with other gases, can be detected by absorbing it in spongy palladium, from which it can be recovered by the action of heat.

## WATER

**196. The Composition of Water.**—The history of the relations of mankind with the substance water would be a task for a lifetime. Happily, we need here to record only the efforts of mankind to discover its nature and composition. Water was for a long time considered to be an elementary body. The first evidence that it was a compound was obtained in the later part of the eighteenth century. Macquer, in 1776, noticed that the hydrogen flame deposited a dew

on cold surfaces, and Priestley, in 1781, noticed the deposition of moisture when a mixture of 'inflammable air' and 'dephlogisticated air' (hydrogen and oxygen) was detonated in a closed vessel by an electric spark. These results were not however followed up. In 1789, van Troostwijk and Deiman noticed that bubbles of gas were produced when an electrical current obtained from a frictional machine was passed through water. Henry Cavendish, one of the most remarkable of the earlier chemists, followed up Priestley's experiment by exploding mixtures of hydrogen and oxygen in closed vessels. In his own words :—

"In order to examine the nature of the matter condensed on firing a mixture of dephlogisticated and inflammable air, I took a glass globe, holding 8,800 grain measures, furnished with a brass cock and an apparatus for firing air by electricity. This globe was well exhausted by an air pump, and then filled with a mixture of inflammable and dephlogisticated air, by shutting the cock, fastening a bent glass tube to its mouth, and letting up the end of it into a glass jar inverted into water, and containing a mixture of 19,500 grain measures of dephlogisticated air, and 37,000 of inflammable; so that, upon opening the cock, some of this mixed air rushed through the bent tube and filled the globe.[1] The cock was then shut, and the included air fired by electricity, by which means almost all of it lost its elasticity.[2] The cock was then again opened, so as to let n more of the same air, to supply the place of that destroyed by the explosion, which was again fired and the operation continued till almost the whole of the mixture was let into the globe and exploded. By this means, though the globe held not more than the sixth part of the mixture, almost the whole of it was exploded therein without any fresh exhaustion of the globe. . . . The liquor condensed in the globe, in weight about 30 grains . . . consisted of water united to a small quantity of nitrous acid."

The latter acid was not found when air was used instead of oxygen, and was derived from impurities in the oxygen used.

Cavendish did not, however, realise the significance of his discovery, for he believed that the gases contained the water before they combined and that it was merely set free, not formed. Lavoisier, however, heard of Cavendish's experiments. To his credit is the fact that he at once saw that they proved that water was composed of hydrogen and oxygen; to his discredit is the fact that he published this without acknowledging his debt to Cavendish. He confirmed the composition of water by passing steam over heated iron, so obtaining hydrogen.

This work established the composition of water *synthetically*; it was soon confirmed *analytically* by Nicholson and Carlyle in the year 1800. These workers electrolysed water and obtained hydrogen

[1] In order to prevent any water from getting into this tube, while dipped into water to let it up into the glass jar, a bit of wax was stuck upon the end of it, which was rubbed off when raised above the surface of the water.

[2] *I.e.*, gaseous state.

and oxygen. Davy further investigated the question and found that water was decomposed by the electric current forming two volumes of hydrogen and one volume of oxygen, and no other product.

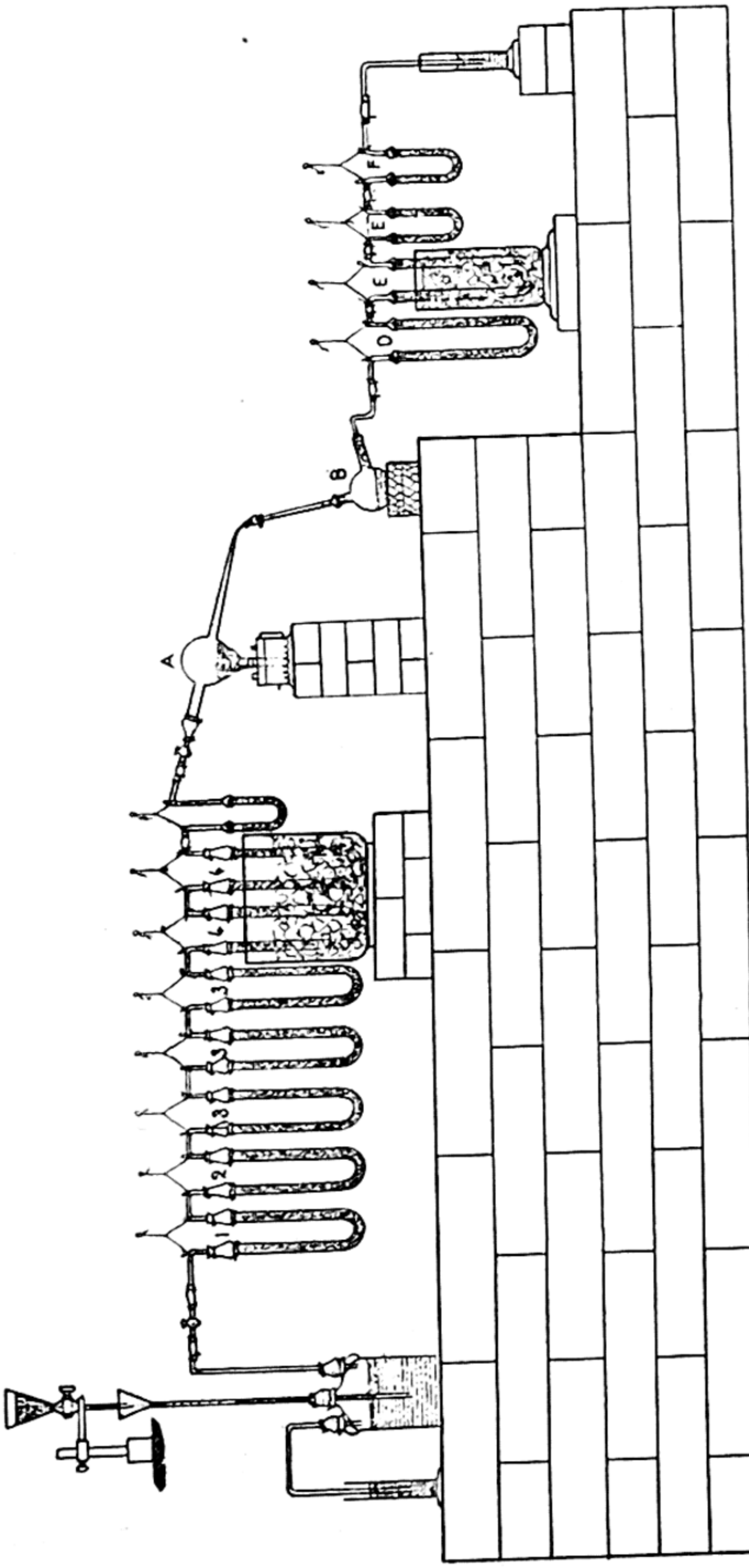



FIG. 66.—Dumas' determination of the gravimetric composition of water.

These facts did not give the formula of water, for there was not, at the period of these experiments, any known connection between volumes of gases and number of atoms.

Rough attempts were made to determine the *weights* of hydrogen and oxygen contained in water by deducing the weights of the gases combining in an experiment such as Cavendish's, by multiplying their volumes by their densities. No very accurate results were obtained, owing to the difficulties of determining the densities with accuracy, using the somewhat primitive types of apparatus then available.

A totally different type of determination was carried out by Dumas in 1842. It is of great interest as the forerunner of all accurate atomic weight determinations. It was, however, of an accuracy inferior to modern determinations such as those of Morley and Noyes, but much superior to any previous determinations.

Hydrogen was prepared from zinc and sulphuric acid and purified by passage through numerous U-tubes, containing: (1) glass moistened with lead nitrate solution to remove hydrogen sulphide; (2) silver sulphate solution to remove arsine and phosphine; (3) three U-tubes containing potassium hydroxide to remove all acid gases ($CO_2$, $SO_2$, $NO_2$, etc.); (4) two U-tubes containing phosphorus pentoxide to remove all traces of moisture. These were immersed in a freezing mixture. Next followed a U-tube containing phosphorus pentoxide, which was weighed before and after the experiment and which, if it showed no change of weight, bore witness that no moisture was contained in the gas.

The gas next passed through a bulb A, previously weighed while exhausted and containing well-dried copper oxide. When heat was applied to the oxide the hydrogen was oxidised to water which passed on as steam and was condensed in the weighed bulb B, and the weighed drying tubes D, containing potassium hydroxide, and E, containing phosphorus pentoxide. The tube F, also containing phosphorus pentoxide, was not weighed and, with the mercury trap, served to protect the apparatus from the moisture of the external air.

The change in weight of the bulb A gave the weight of oxygen lost by the copper oxide, and the change in the weights of the bulb and tubes B, D, E gave the weight of water formed.

As a mean of nineteen experiments Dumas found :—

| | |
|---|---|
| Oxygen lost by copper oxide. . . | 44·22 gms. |
| Water produced . . . . . | 49·76 gms. |
| Hydrogen contained in water (by difference) | 5·54 gms. |

Thus the ratio of hydrogen to oxygen in water was 5·54 : 44·22 or 1 : 7·98 by weight. Dumas himself believed that the ratio was actually 1 : 8, but in fact the error is in the other direction, and 1 : 7·94 would be closer.

It was then known that water contained 1 volume of oxygen to 2 volumes of hydrogen and (nearly) 8 parts by weight of oxygen to 1 part by weight of hydrogen.

It was assumed at first that water had the formula HO, and that the atomic weight of hydrogen was one and that of oxygen eight. We now know that this was incorrect, but it gave quite satisfactory results in most respects. If we call the atomic weight of oxygen eight we are in effect giving the symbol O to a half-atom of oxygen. Thus the formula HO with O = 8 has the same quantitative meaning as $H(O)_{\frac{1}{2}}$ with oxygen = 16, or in fact as $\frac{1}{2}(H_2O)$.

Thus these formulæ represented the *proportions* of the elements contained in the molecules correctly, but were sometimes wrong in the number of molecules. Thus the equation for the action of zinc upon steam as written before 1860 was,

$$2HO + Zn = ZnO_2 + 2H\,;\ (O = 8)\,;$$

using modern atomic weights this is written,

$$H_2O + Zn = ZnO + H_2\,;\ (O = 16)\,;$$

but both equations indicate quite correctly the weights of the materials formed.

It had long been known that there was a connection between densities of gases and their formulæ and reacting volumes (cf. §§ 45, 46), and while Avogadro's hypothesis, proposed in 1814, explained these relationships well enough in a great many cases, in others it broke down completely.

Cannizzaro, in 1857, put forward more strongly an idea that Gerhardt had proposed in 1842, that oxygen and the elements of which the atomic weights were based on oxygen should have their atomic weights doubled. This process at once made Avogadro's

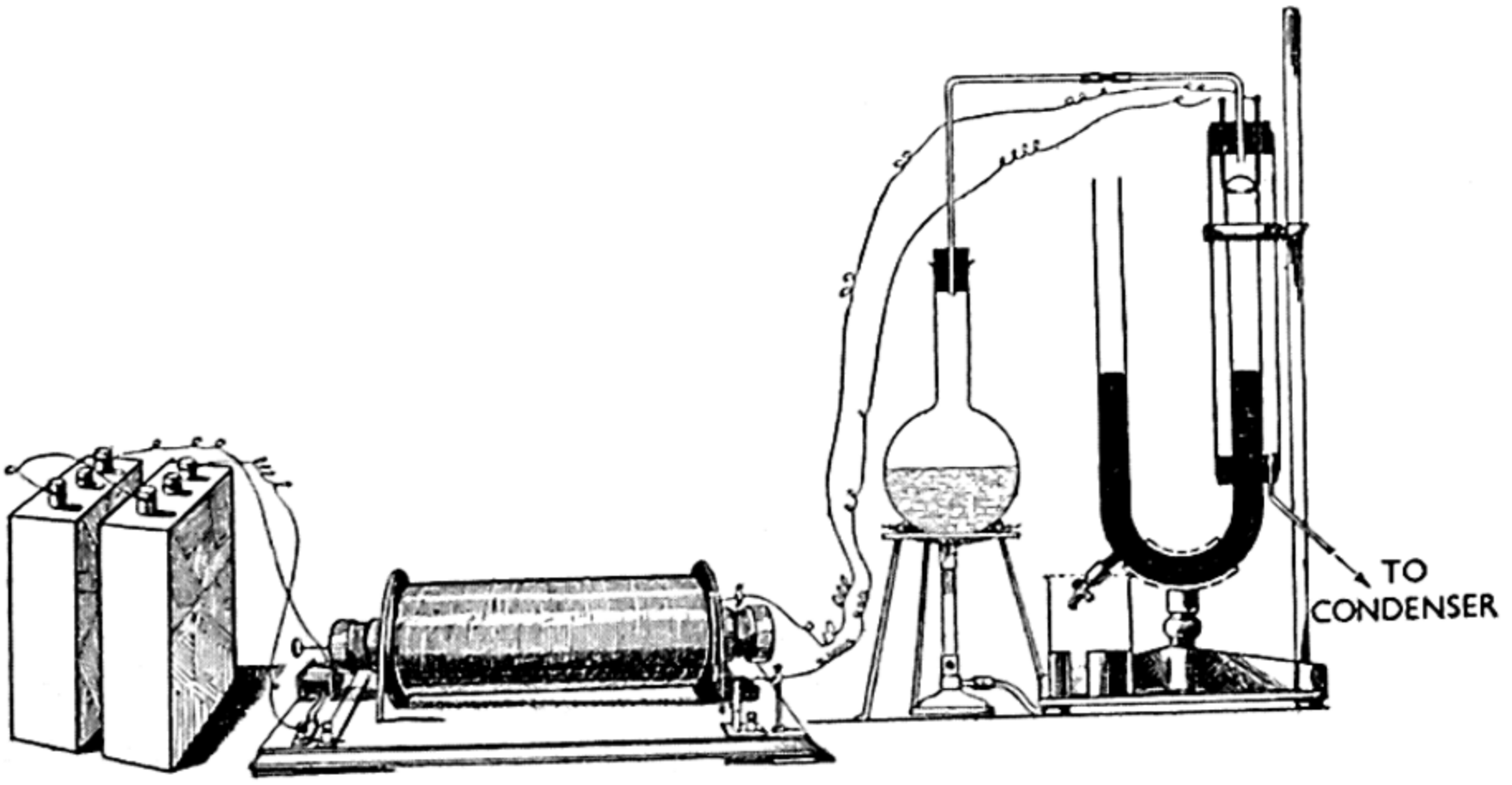



FIG. 67.—Volume composition of steam.

hypothesis correct for all known cases, and accordingly oxygen was given the atomic weight 16, and the number of atoms of it in every formula was halved. Thus water, instead of HO became $H_2O$.

Assuming Avogadro's hypothesis, it was evident that the formula of hydrogen was $H_2$ (§ 48), and experiments on the volume composition of water further confirmed its formula. The atomic weight of oxygen being taken as 16, its density (16, $H_2 = 1$, *v.* § 50) showed that its formula was $O_2$.

Gay-Lussac had, in 1808, performed an experiment, later modified by Hofmann (1865), which clearly showed the volume relationships between hydrogen, oxygen and steam and so helped to confirm the formula $H_2O$.

A graduated eudiometer—a stout U-tube fitted with electrodes for firing gases by a spark—is surrounded by a jacket through which can be passed amyl alcohol vapour so as to maintain it and the gases contained therein at 132° C. A mixture of hydrogen and oxygen in the proportions of 2 : 1 by volume is placed in the sealed limb of the tube. The tube is then heated by the vapour and the volume of the hot gases read off on the gradations of the eudiometer. The open limb of the U-tube is corked and the mixture of gases is fired. The steam formed by the explosion does not condense at 132° C. and its volume is read off. It is found that two volumes of hydrogen combine with one volume of oxygen to form two volumes of steam. If we adopt Avogadro's law it follows that two molecules of hydrogen and one molecule of oxygen form two molecules of water. We know that hydrogen is $H_2$ and oxygen is $O_2$, so

$$2H_2 + O_2 = 2H_mO_n,$$

and the only formula for steam which can satisfy this equation is $H_2O$.

**197. Occurrence.**—Water is found in vast quantities in the sea, rivers, etc., and as moisture saturating the soil. The air normally contains from 1–5 per cent. of its vapour. All living things contain a high proportion of water. A cucumber contains 97 per cent., a man 60 per cent. of water. All substances which have been exposed to the air absorb some moisture. An apparently dry powder, such as powdered glass, will always lose a little moisture when heated, while colloids like wood, paper, wool, etc., absorb very noticeable quantities of water from the air. For this reason no chemical material which does not react with water is ever found to be free from water unless it has been specially dried.

**198. Sources of Water.**—Water is so abundant that it is never made by chemical methods. It is, however, a frequent product of chemical actions, being produced :—

(*a*) When hydrogen or compounds of hydrogen burn in air or oxygen or are passed over heated copper oxide or otherwise oxidised.

(*b*) When acids react with oxides or hydroxides.

The purification of water is a most important matter in view of the influence of a pure water supply upon public health. For purposes of town supply a chemically pure water is neither obtainable nor desirable ; what is required is water free from any impurities which may make the water dangerous to health, unpalatable, or unsuitable for industrial use.

Water for purposes of town supply is derived as a rule from wells or from rivers or lakes. In any case, the water may be regarded as being derived ultimately from rain. Rain water is nearly chemically pure, containing as impurities traces of dissolved gases, nitrogen, oxygen, carbon dioxide, ammonia, nitrous acid, nitric acid, and in large towns sulphurous and sulphuric acid. Rain carries down with it also dust particles and a minute proportion of sodium chloride derived from dried sea spray. The amount of impurity other than gases does not reach more than about 5 parts per million. Water is so universal a solvent that rain water takes up impurities from the ground as soon as it reaches it. Rain water may run off the ground as *surface water* and collect in streams or rivers, or may penetrate deeply into the soil and underlying strata to emerge as *spring water* or *well water*.

*Surface water* varies much in quality and purity. If it has flowed from mountain areas of granite, clothed only with a layer of peat, containing little mineral matter, the water which is collected in lakes or dams may be little less pure than rain water. Thus the water supplied to Glasgow from Loch Katrine contains only about 3 parts of solid matter in 100,000 of water. Surface water in agricultural, and still more in thickly-populated districts, is much less pure and contains both organic and mineral matter derived from the soil. Typical samples might contain from 5–100 parts of solid matter per 100,000, varying with the type of soil traversed.

*Spring water* has usually filtered through finely porous soil or rock for some distance before emerging and is consequently fairly free from bacteria, etc. In England numbers of springs are found at the foot of our numerous chalk hills. The water filters through the porous chalk and emerges into the greensand which often underlies it, and where this stratum is exposed springs are numerous. Such water as this is always hard (see below) and may contain some 25–50 parts of solid matter per 100,000, mainly calcium compounds.

*River water* is partly spring water and partly surface water. It

usually contains a good deal of mineral matter and often a vast population of bacteria, infusoria and other low forms of life. Such water may contain from 1,000 to 1,000,000 bacteria per cubic centimetre, largely forms derived from sewage. Most of these are, fortunately, harmless, but if sewage reaches the river at all, such bacteria as those which cause cholera and typhoid will, when these diseases are prevalent, also reach river water in a living condition. Thus, if a town is forced to drink river water, as is London, such water must be adequately purified by filtration and storage or otherwise.

*Well water* from shallow wells is not very satisfactory. Such wells are filled by water soaking in from the neighbouring soil and may consequently be contaminated with sewage from cesspools, leaky sewers, etc. The water from shallow wells usually contains much mineral matter, commonly 100 parts per 100,000 and often more. Such water is often exceedingly hard.

Deep wells, such as those which are driven deep into the chalk or down to the greensand below it, give water which is freed from bacterial contamination by filtration through masses of porous chalk. Such water is very hard as a result of its prolonged contact with the chalk.

**199. Purification for Town Supply.**—Such waters as are derived from deep wells or from high moorland surface streams require no purification.

River water, such as that used in London, is allowed to filter through beds of sand resting on stones and gravel. A slimy layer of clay, algæ, bacteria, etc., is formed on the surface of the sand, and the pores of this material are so fine as to remove almost all suspended matter. Certain experiments showed that if the water entering the filter contained 31,200 bacteria per cubic centimetre, that leaving it contained only 122 in the same volume.

The filter does not, of course, remove dissolved mineral matter, but, unless this is present in great quantity, it is impracticable and indeed unnecessary to remove it from a town supply.

The chief substances found dissolved in river and well water are :

(*a*) The bicarbonates of calcium and, occasionally, magnesium.

(*b*) The sulphates and, occasionally, the chlorides of the above metals.

The first of these impurities arises from the action of water containing dissolved carbon dioxide upon the calcium carbonate of the chalk or limestone rocks which it has traversed. The soluble calcium bicarbonate is formed,

$$CaCO_3 + H_2CO_3 = Ca(HCO_3)_2,$$

and the resulting water may contain up to 50 parts or more per

100,000 of calcium carbonate. Magnesian limestone containing magnesium behaves in a similar way and water derived from it contains magnesium bicarbonate.

Calcium sulphate is a common mineral and is perceptibly soluble in water (1 : 500) and is accordingly often found in water.

The removal of these substances from water is carried out on the large scale by the excess lime process and the permutit process (§ 200).

Water also contains traces of ammonia and nitrates derived from nitrogenous organic impurities and also from the rain water which is the original source of all forms of water. Traces of sodium chloride are (except near the sea) derived chiefly from animal excretions. Water containing much chloride is, therefore, to be regarded with suspicion.

**200. Hard Water.**—Water which reacts with soap and produces an insoluble precipitate is said to be *hard*. Water containing salts of calcium or magnesium, or, indeed, of any of the metals other than sodium and potassium, has this property. Soap consists of sodium stearate, oleate, palmitate, etc., and the precipitate formed consists of these salts of calcium, magnesium, iron or the metal in question. We may, for the sake of example, regard soap as consisting of *sodium stearate*, which is soluble in water ; this reacts with any soluble calcium salt according to the equation,

$$2Na\overline{St} + Ca(HCO_3)_2 = 2NaHCO_3 + Ca\overline{St}_2,$$

where $\overline{St}$ is the stearate radical $C_{17}H_{35} . COO^{--}$.

Hard water is therefore obviously unsuitable for washing purposes, for until the calcium in the water has been removed by reacting with the soap, none of the latter remains in solution, and so cannot exert its detergent powers. Hard water accordingly causes great wastage of soap.

Water which contains the bicarbonates of calcium and magnesium may be freed from them by boiling and is said to be *temporarily hard*. The bicarbonate decomposes when heated and calcium or magnesium carbonate is deposited both as a precipitate and as a crust on the sides of the containing vessel,

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

This occasions grave inconvenience in domestic hot-water boilers, steam boilers, etc., which require cleaning at comparatively short intervals where such water is used (see Plate XI.).

The inconveniences of hard water have led to the development of processes designed to remove from water the substances which cause its hardness. There are four chief methods of water-softening in use.

(*a*) The domestic process is the addition of sodium carbonate (washing soda, bath salts), or sometimes ammonia to the water. In the first case all the calcium and magnesium are precipitated as carbonates,

$$Ca(HCO_3)_2 + Na_2CO_3 = 2NaHCO_3 + CaCO_3 \downarrow$$
$$CaSO_4 + Na_2CO_3 = Na_2SO_4 + CaCO_3 \downarrow$$

or
$$Ca^{++} + CO_3^{--} \rightarrow CaCO_3 \downarrow .$$

In the second case only the bicarbonates are decomposed, but other salts are not affected.

$$Ca(HCO_3)_2 + 2NH_4OH = (NH_4)_2CO_3 + CaCO_3 \downarrow + 2H_2O$$

These methods are much too expensive for softening the water

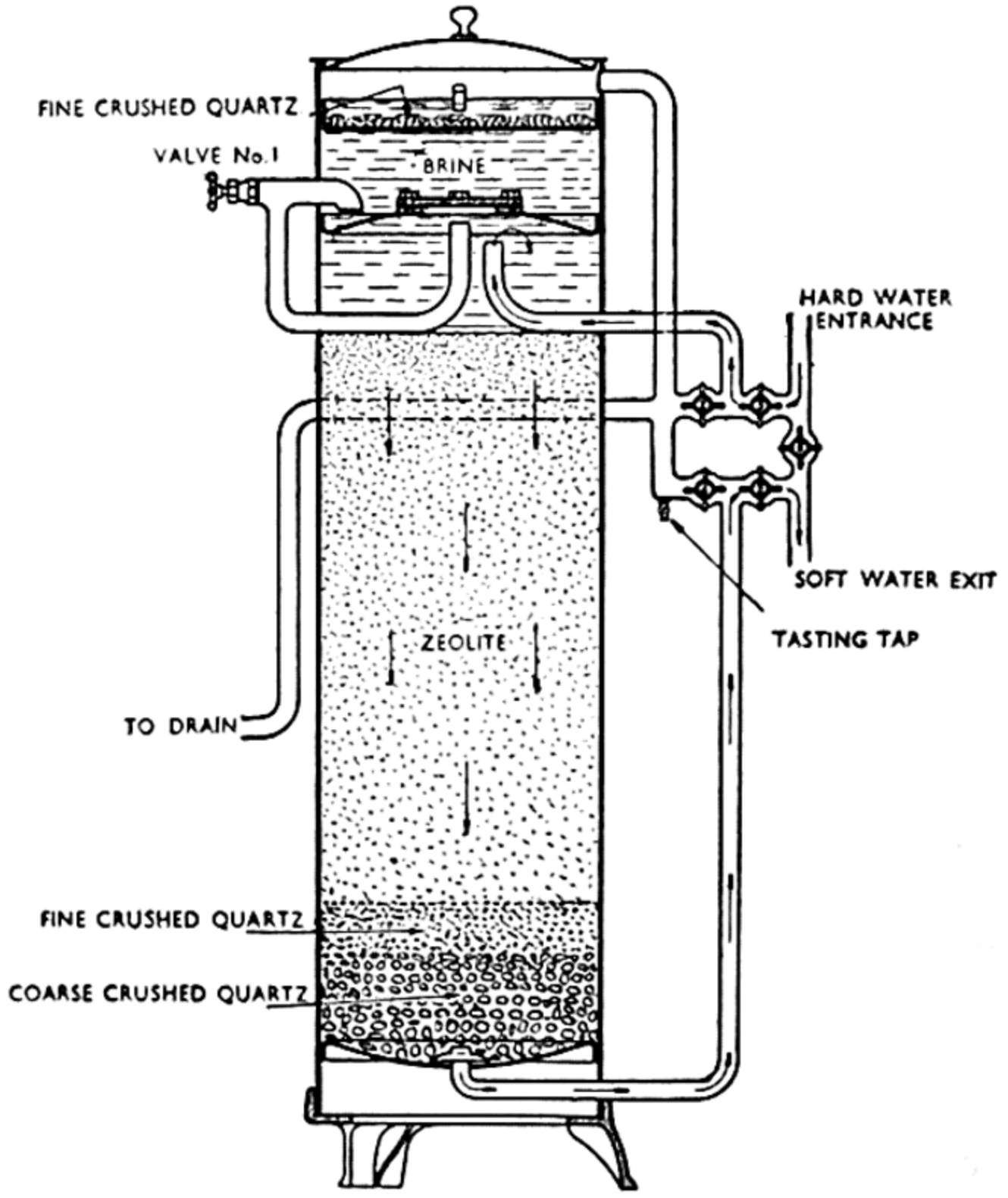



FIG. 68.—Illustrates the plant supplied by Messrs. Electrolux, Ltd., Luton, for domestic water softening.

(i) *Water softening.*—Valves 3 and 5 open: remainder shut. Course of water shown by arrows. (ii) *Reverse flush.*—Valves 2, 5 and 6 open: remainder shut. To lift softening bed. (iii) *Regeneration.*—Valve 6 open (to give a supply to house). Valves 1 and 4 open: remainder shut. Salt water containing calcium chloride passes through zeolite to drain. (iv) *Washing out salt.*—Valves 6, 3 and 4 open: remainder shut. Water washes out salt and calcium chloride to drain. When the water passing off tastes fresh, valves are set to position (1) (water softening) once more.

supply of a whole town. Soda is sometimes added to the water used in steam boilers.

(*b*) The excess lime process is in use at Canterbury, Southampton, Caterham and some other places. The process removes temporary hardness only and depends on the reaction between calcium bicarbonate and calcium hydroxide.

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 \downarrow + 2H_2O.$$

It is, of course, essential that the lime should be added in the exact quantity needed, for an excess of lime would make the water harder than before.

The lime, in the form of milk of lime or lime water, is added to the water, contained in large tanks. The water becomes cloudy and in about two to three hours the precipitate of the carbonate settles out sufficiently well to allow the surface water to be drawn off.

(*c*) The process which is most efficient and most widely used is the base-exchange or permutit process. This is never used to soften a whole town's supply, but a softening plant is attached to the water inlet pipe of an individual private house or factory. The softening is accomplished by allowing the water to flow over a bed of granulated hydrated sodium aluminium silicate. This substance may be made artificially—' permutit,' but is usually obtained from a native mineral—zeolite. The commonest form of this zeolite is greensand. A reaction takes place between the zeolite and the calcium and magnesium salts of the water (which we will regard for the purposes of the equation as calcium bicarbonate), resulting in the

$$Ca(HCO_3)_2 + Na_2Al_2Si_2O_8 \,.\, xH_2O = CaAl_2Si_2O_8 \,.\, xH_2O + 2NaHCO_3$$

conversion of the sodium aluminium silicate into calcium aluminium silicate, while sodium bicarbonate goes into solution. The issuing water contains no calcium or magnesium salts and the trace of sodium present is quite innocuous. After a few days the zeolite becomes so far converted into the calcium compound that it will remove no more calcium from the water.

The zeolite is then regenerated by running over it for five minutes a concentrated solution of common salt. The high concentration of this causes the reverse reaction to proceed almost to completion (§ 110) ;

$$2NaCl + CaAl_2Si_2O_8 \,.\, xH_2O \rightleftharpoons CaCl_2 + Na_2Al_2Si_2O_8 \,.\, xH_2O,$$

the sodium zeolite is once more formed and the calcium goes into solution as the chloride and is run to waste. The zeolite can then again be used to soften more hard water until it once more needs regeneration.

(*d*) *Softening by means of metaphosphates.*

An important new development in water-softening has been

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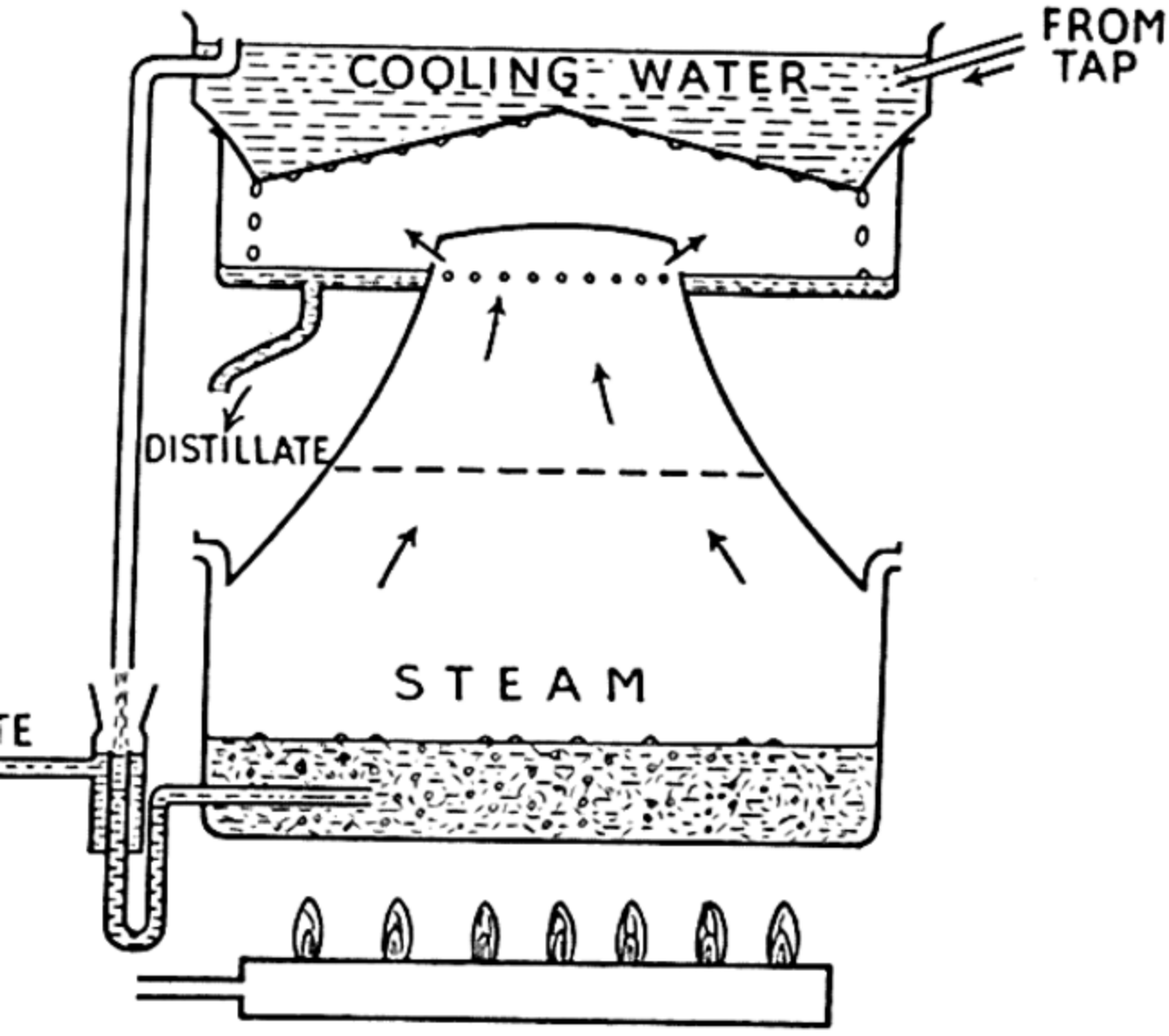


FIG. 69.—Dome-still for distillation of water.

the introduction of sodium hexa-metaphosphate (sold as Calgon). The formula of sodium metaphosphate is usually given as $NaPO_3$, but apparently several polymers exist; the material used for water-softening consists chiefly of the hexa-metaphosphate $Na_6P_6O_{18}$. This salt contains some of the metal in the acid radical, and has the formula $Na_2[Na_4P_6O_{18}]$. It reacts with calcium ions to form a *soluble* complex salt in which the calcium is not present as calcium ion, and which therefore gives no precipitate with soap.

$$2CaX_2 + Na_2[Na_4P_6O_{18}] \rightleftharpoons 4NaX + Na_2[Ca_2P_6O_{18}]$$
$$2Ca^{++} + [Na_4P_6O_{18}]^{--} \rightleftharpoons 4Na^{+} + [Ca_2P_6O_{18}]^{--}$$

Since the sodium hexa-metaphosphate takes up calcium ions from solution, it will dissolve calcium compounds which are insoluble in water (*e.g.*, boiler-scale or the lime-soap which encrusts badly washed textiles). The substance has found wide use in treatment of boiler feed-water, in laundry work, wool-scouring, and domestic washing powders.

**201. Purification of Water for Scientific Purposes.**—Water for scientific purposes is in practice required of two degrees of purity :—

(*a*) Distilled water of high purity.

(*b*) "Conductivity" water of the highest purity obtainable.

Distilled water is rarely prepared with the ordinary distilling flask and Liebig condenser. The ordinary laboratory water-still is either a combined water-oven and still or some type of dome-still, one of the many patterns of which is illustrated in Fig. 69. Water from such a still is pure enough for all ordinary chemical work; but it contains traces of salts, etc., and for physico-chemical purposes, notably the determination of the electrical conductivity of solutions, it is not pure enough. Water dissolves sufficient alkali from the surface of glass to render it useless for work of this type, and many methods have been devised to produce water of very high purity.

Very pure water is best obtained by adding a little acidified

potassium permanganate solution to ordinary distilled water and allowing the mixture to stand for a few hours. The water is then distilled ; the distillate is mixed with a little barium hydroxide and redistilled. The distillate is then finally distilled, using a solid tin condenser, and the pure water is collected in a flask of hard glass which has been steamed or repeatedly treated with water to remove all soluble alkali. The water so obtained still contains gases, and if these impurities are considered deleterious the final distillation must be conducted *in vacuo* (Fig. 71). The chief undesirable gaseous impurity is carbon dioxide, and this is often removed by conducting the distillation in a current of carbon dioxide free air.

**202. Physical Properties.**—Water is at ordinary temperatures a liquid which, while it appears colourless in small quantities, is blue when viewed through considerable depths. Water is without taste and smell. Many of the properties of water are taken as the numerical standards of comparison. Thus water freezes at 0° C. at standard atmospheric pressure (+ ·0076° C. under its own vapour pressure), and boils at 100° C. ; its density at 4° C. taken as unity.

The specific heat of water is taken as unity 1·000, or in other words, 1·000 calorie is the quantity of heat required to raise the temperature of a gram of water by one degree. Since the specific heat varies with the temperature the degree in question must be specified. Thus the temperature of 1 gm. of water is raised by 1 *zero calorie* from 0–1° C., by a 15° *calorie* from 14·5° C. to 15·5° C. ; a *mean calorie* is one hundredth part of the heat needed to raise the temperature of 1 gm. of water from 0° C. to 100° C.

The coefficient of expansion of water varies remarkably with the temperature. Water actually *contracts* when heated from 0° C. to 4° C., and from 4° C. to 100° C. expands. This peculiar property may be due to the form $(H_2O)_3$ changing with rising temperature into the denser $(H_2O)_2$.

Water is a very poor electrical conductor, the pure liquid having a specific conductivity of $0{\cdot}04 \times 10^{-6}$ mhos. at 25° C. Thus a column of water a centimetre long has the same resistance as a rod of copper of the same cross-section and nearly 90 million miles long.

The physical properties of water are in strong contrast to those of its nearest chemical analogue, hydrogen sulphide.

While we should expect water to have a lower boiling-point than hydrogen sulphide we find actually that its boiling-point is higher than that of any hydride of Group VI. B. This anomalous behaviour is believed to be due to its association into aggregates of molecules, and is paralleled in the relationship of hydrogen fluoride to the other hydrogen halides (§ 1034).

Liquid water is somewhat polymerised, loose aggregations of water molecules being continually formed and decomposed.

The evidence for this belief that the molecules of water are associated depends on (*a*) the abnormally high density of steam just above the boiling-point; (*b*) the fact that water boils at 100° C. while its analogue, $H_2S$, which would be expected to boil at a higher temperature, boils at − 61° C; (*c*) its parachor value [1]; (*d*) many departures from the physical properties to be expected from a substance of the simple formula $H_2O$ and the low molecular weight of 18.

Water is remarkable as being an *ionising solvent*, *i.e.*, a solvent in which many polar compounds—acids, bases, and salts—dissolve and become dissociated into ions. Water is not the only ionising solvent; others include formic acid, hydrogen cyanide, liquid sulphur dioxide, liquid ammonia.

In general, it is found that ionising solvents are liquids with high dielectric constants. There does not appear to be an exact relationship between dielectric constant and ionising power, but the properties are clearly connected.

Ionising solvents all appear to be *donors*, *i.e.*, some atom in their molecule has two or more valency electrons, which are not shared with other atoms Recent work seems to indicate that ionisation is always accompanied by combination of the solvent and one or more of the ions. This, if correct, explains the necessity for an ionising solvent to have donor or acceptor properties.

Water is itself dissociated, forming a very small proportion of hydrogen and hydroxyl ions,

$$H_2O \rightleftharpoons H^+ + OH^-.$$

The evidence for this fact is its conductivity and the satisfactory explanation of the phenomena of hydrolysis (§ 121). The proportion of these ions is such that the product of their concentrations (gram-equivalents per litre) is approximately $10^{-14}$,

$$[H^+]\,[OH^-] = 10^{-14}.$$

From this fact many interesting deductions concerning the phenomena of hydrolysis and precipitation can be gained.

**203. Chemical Properties of Water.**—The chemical properties of water are chiefly to be classified as—

(*a*) Reactions involving its decomposition.
(*b*) Catalytic actions.
(*c*) Formation of molecular compounds.

[1] The parachor of a substance is given by the formula $\frac{M}{D-d}\gamma^{\frac{1}{4}}$, where M is the molecular weight of a liquid, D and d the densities of the liquid and its vapour, and $\gamma$ its surface tension. The parachor can be readily computed by simply adding together a series of numbers representing the various atoms and valency linkages present in the molecule. If the parachor is experimentally determined, the value obtained can be used to determine how many atoms and what valency linkages are present in the molecule.

Water is decomposed when heated to very high temperatures in accordance with the reaction,

$$2H_2 + O_2 \rightleftharpoons 2H_2O + 116{\cdot}2 \text{ cals.}$$

It follows that since heat is absorbed in the decomposition of water it will take place most completely at high temperatures. Actually, while at 1 atmospheric pressure and 1,000° C. only about ·000026 per cent. is decomposed, at 2,000° C., about 0·6 per cent. is broken up, while at 3,500° C. some 30 per cent. is decomposed.

The fact of its decomposition is difficult to demonstrate, since it takes place only at high temperatures and recombination takes place as a rule before the gases are cool enough for the hydrogen and oxygen formed to be detected. Several devices have been employed to illustrate this decomposition, of which that of A. Holt (Fig. 70) is one of the most satisfactory.

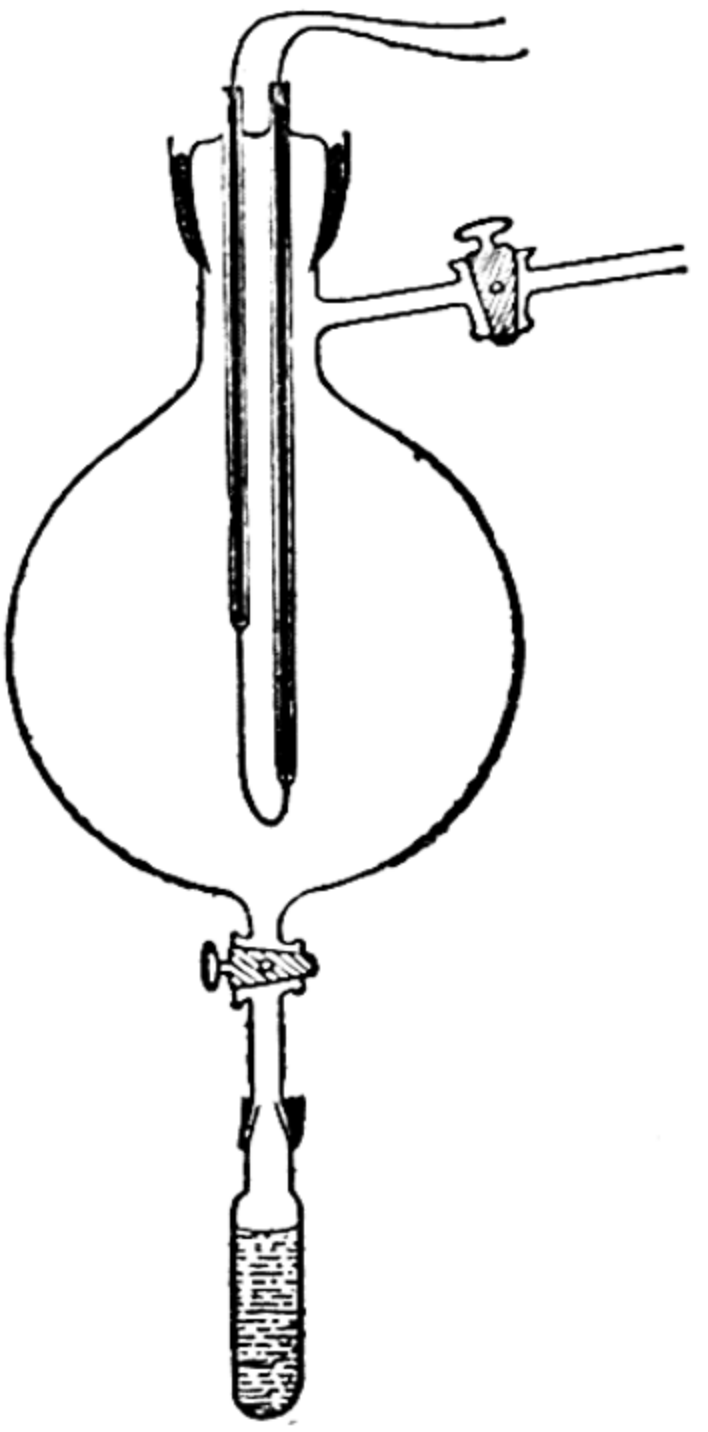

FIG. 70.—Decomposition of water vapour by heat.

A platinum wire was heated to 1,200–1,600° C. in an atmosphere of water vapour at low pressure. The white-hot wire caused the vapour to decompose, but at the low pressure used the gases diffused rapidly away from the wire before much recombination could take place. After some time the gases were pumped off, and after the water vapour had been condensed by a freezing mixture hydrogen and oxygen remained behind. The degree of dissociation did not exceed 6 parts in 10,000 even at c. 1,630° C.

Water is decomposed when it is treated at suitable temperatures with certain elements which are more electropositive than hydrogen.

The alkali metals (*q.v.*) decompose liquid water in the cold as also do the metals of the alkaline earths,

$$2K + 2H_2O = 2KOH + H_2$$
$$Ca + 2H_2O = Ca(OH)_2 + H_2.$$

The action of magnesium on cold water is comparatively slight. Hot water is fairly quickly attacked by magnesium, beryllium and the rare-earth metals.

Magnesium, zinc and iron readily decompose steam. The former

burns in steam and the latter two decompose it at a red heat. Aluminium is protected by a film of oxide from the action of water, but if this is removed and prevented from re-forming by amalgamation with mercury it decomposes water in the cold. Nickel and cobalt, tin, cadmium and osmium also decompose water at a red heat to varying extents. Lead and copper only decompose water at a white heat, while mercury, silver, gold and the platinum metals, except osmium, have no effect upon water.

Of the non-metals only carbon, silicon, fluorine and chlorine react. The first forms carbon monoxide and hydrogen at a red heat,

$$C + H_2O \rightleftharpoons CO + H_2.$$

The action of silicon is similar. At a red heat amorphous silicon reacts slowly with water, forming the oxide, silica,

$$Si + 2H_2O = SiO_2 + 2H_2.$$

Fluorine forms hydrogen fluoride and liberates oxygen, mixed with some ozone,

$$2F_2 + 2H_2O = 4HF + O_2.$$

Chlorine behaves analogously. It forms hypochlorous and hydrochloric acids,

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl,$$

but when exposed to light the reaction,

$$2Cl_2 + 2H_2O = 4HCl + O_2$$

takes place.

Among the numerous reactions of compounds with water, we may note the following :—

(*a*) Certain acidic and basic oxides (anhydrides) form acids and alkalis respectively with water,

$$SO_3 + H_2O = H_2SO_4$$
$$CaO + H_2O = Ca(OH)_2.$$

(*b*) "Hydrolytic" reactions. Many halides, especially those of non-metals and acidic groupings of atoms, react with water, forming hydrogen halides and the hydroxide of the element or grouping. We may instance the reactions of phosphorus trichloride and sulphuryl chloride with water,

$$PCl_3 + 3H \,.\, OH = \underset{\text{Phosphorous acid.}}{P(OH)_3} + 3HCl$$

$$SO_2Cl_2 + 2H \,.\, OH = \underset{\text{Sulphuric acid.}}{SO_2(OH)_2} + 2HCl.$$

The halides and other salts of metals are often hydrolysed by water, the hydroxide of the metal or a basic salt being formed together with the free acid. Thus antimony trichloride with a large excess of water yields first oxychloride and then the oxide,

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl,$$
$$2SbOCl + H_2O \rightleftharpoons Sb_2O_3 + 2HCl,$$

and bismuth trichloride yields bismuth oxychloride only,

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$

Ferric sulphate forms a basic salt of uncertain composition,

$$Fe_2(SO_4)_3 + 2H_2O = 2Fe(OH)SO_4 + H_2SO_4.$$

Pure water is hardly affected by the electric current because the proportion of ions it contains is so small that the quantity of electricity they can carry is almost negligible. If, however, there is added to the water any substance which yields ions which are stable and less readily discharged than hydrion or hydroxyl ion, the added ions carry the current, while hydrion and hydroxyl ions are discharged, giving hydrogen and oxygen. The fact that only a minute proportion of these ions are present does not matter, for as fast as they are used up they are replaced by the ionisation of more water. The electrolysis of water in presence of acids and alkalis has already been discussed (§ 181), but as a further example the electrolysis of water between platinum poles in presence of sodium sulphate may be considered.

*Cathode.* The sodium ions $Na^+$ travel to the cathode, carrying the current. Hydrions are discharged giving *hydrogen* and their place is supplied by water molecules ionising. Each water molecule gives a hydrion and a hydroxyl ion. The latter remain and, together with the sodium ions, accumulate round the cathode, constituting a solution of sodium hydroxide.

*Anode.*—The sulphate ions $SO_4^{--}$ travel to the anode, carrying the current. Hydroxyl ions are discharged giving water and oxygen. These are replaced by the ionisation of water molecules. The hydrion formed at the same time accumulates round the anode.

If the liquid is stirred the hydroxyl ions and hydrions from the cathode and anode respectively reunite, forming water, and the only final change is the decomposition of some of the water into hydrogen and oxygen.

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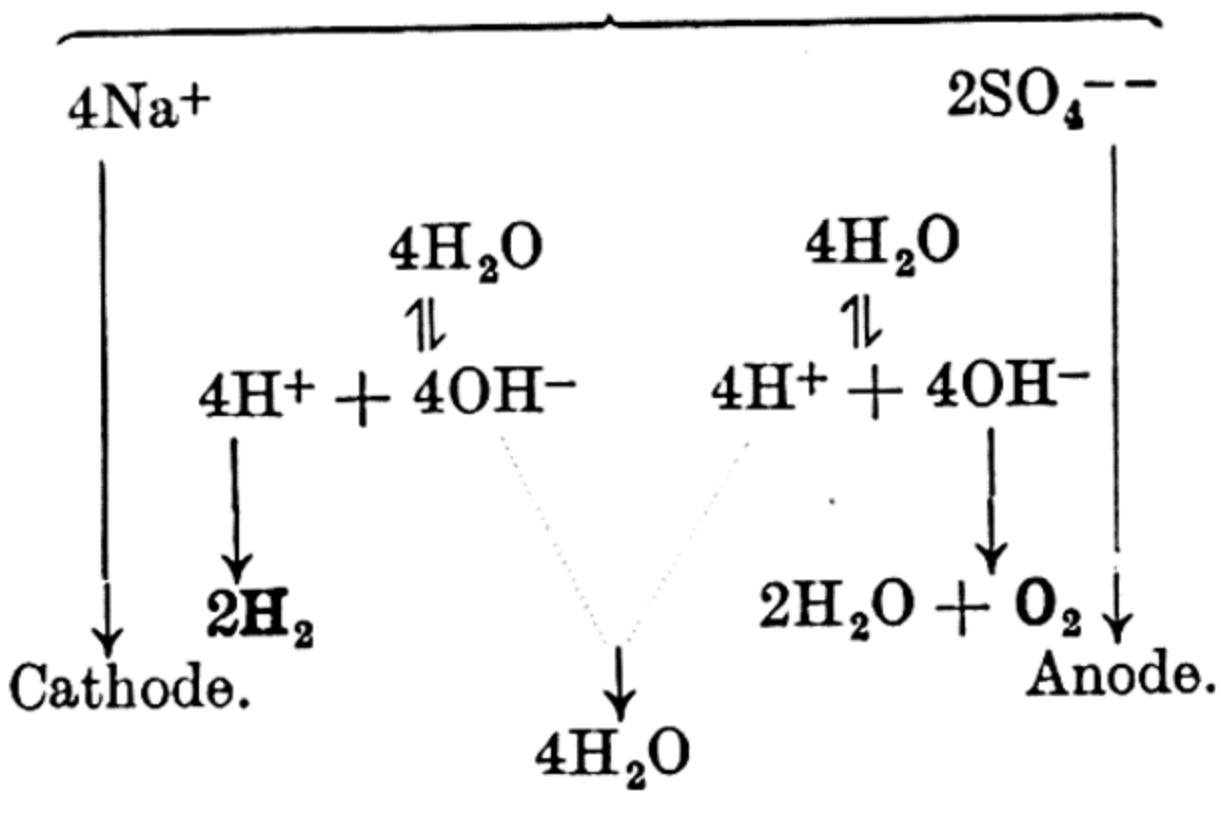
*Sodium Sulphate Solution.*




**204. Water as a Catalyst.**—It has been known for many years—in fact, since the eighteenth century—that certain chemical reactions proceed more rapidly in presence of water. The absorption of carbon dioxide by lime, the oxidation of phosphorus and iron by oxygen, the reduction of gold salts by hydrogen were all known to take place slowly or not at all in what was then considered to be the absence of moisture.

Actually, an appreciable amount of water was certainly present in the materials used in all these reactions which, indeed, only take place in presence of considerable moisture. These observations did not attract much attention until, in 1880, the discovery was made by Dixon that a mixture of carbon monoxide and oxygen which had been dried over sulphuric acid did not explode when a spark was passed through it. The addition of even a trace of water caused the gases to explode violently when a spark was passed.

Still more remarkable results were obtained by Baker and others when the process of removal of water was carried a stage further.

**205. Intensive Drying.**—The complete drying of a substance is an exceedingly difficult task. Water is obstinately retained by glass surfaces for a long time and very careful technique is required to reach the intense degree of drying obtained in many of these experiments. For this reason the accuracy of much of the work of Baker and others has been disputed by investigators who could not reproduce his results; and, of late years, there has been a growing doubt as to the validity of some of them.

The intensive drying of gases is carried out by drying them as far as possible by passing them over sulphuric acid and phosphorus pentoxide and then sealing them up in bulbs or tubes, and leaving them in contact with phosphorus pentoxide for some months or years. The tubes are best made of silica, though glass is often used.

*Reaction of Hydrogen and Chlorine.*—These gases, when dried so that the water present forms only about one ten-thousand millionth of the whole, no longer combine even in sunlight. When still further dried neither ultraviolet light nor heating to high temperature explodes the gases, though in the latter case some union takes place.

*Reaction of Hydrogen and Oxygen.*—These gases, when intensively dried do not explode at several hundred degrees above their usual ignition temperature.

*Hydrogen Chloride and Ammonia.*—These gases do not combine when intensively dried.

Amongst other reactions catalysed in this way by water are the combination of chlorine and ethylene, sodium and oxygen, sulphur and oxygen, hydrogen chloride and lime, carbon dioxide and lime, and many others.

**206. Explanations of the Inhibition of Reactions by Removal of Water.**—It may at once be said that the explanations of these curious phenomena are hardly satisfactory. It is known that some gas reactions proceed by *chain-reactions* (cf. p. 694) and that water is the catalytic substance. Thus the reaction of carbon monoxide and oxygen may be that indicated by the equations,

(i.) $$CO + H_2O \rightarrow CO_2 + H_2,$$

(ii.) $$2H_2 + O_2 \rightarrow 2H_2O,$$

when water is present, while at higher temperature the direct reaction,

$$2CO + O_2 = 2CO_2$$

may predominate.

Again, films of adsorbed water on the surface of glass vessels may dissolve the reacting substances and so bring them into more intimate contact. The most curious feature is that water is apparently the only substance the removal of which inhibits chemical reactions.

**208. Additive Compounds of Water.**—Water forms numerous molecular compounds (§ 155) with other substances. Water is apparently a saturated substance, but its molecule actually contains two pairs of valency electrons by which it can form co-ordinate linkages with compounds capable of forming such linkages,

$$H : \ddot{O} : H$$

The most important of these molecular compounds are the hydrates.[1] When many acids, bases and salts and a few other compounds are crystallised by cooling or evaporating their solutions, the crystals so produced frequently contain combined water. That this water is combined and not merely admixed is shown by the fact that these hydrates always contain water in simple molecular proportions.

[1] The use of the term, 'hydrate' for 'hydroxide' as in sodium hydroxide is incorrect. The term 'hydrate' should be reserved for these molecular compounds.

Thus all sodium sulphate crystals have one of the following definite formulæ,

$$Na_2SO_4 . 10H_2O,$$
$$Na_2SO_4 . 7H_2O,$$
$$Na_2SO_4,$$

which is sufficient evidence that the water is combined.

These hydrates are usually very unstable compounds, and the different molecules of water in the same compound are held, as a rule, with varying degrees of tenacity. Thus from crystallised copper sulphate $CuSO_4 . 5H_2O$ four molecules of water of crystallisation are driven off at 100° C. or a little above, while the fifth is retained until c. 200° C. is reached. Similar phenomena are shown by many, but not all, other hydrated salts.

The mode of attachment of water of crystallisation has been a source of some difficulty. The distances between the water molecules and the salt ions, as revealed by X-ray studies, is greater than would be expected from a co-ordinate-linkage. The water molecule is a dipole, that is to say one end of it is preponderantly electropositive and the other electronegative: it is thought that the powerful electrical attractions of the ions of the salts cause water molecules to be grouped round them. In agreement with this notion is the fact that salts are more generally and more highly hydrated than non-ionised compounds. Water can be linked to ions by undoubted co-ordinate linkages (as in the cobaltammines *q.v.*): such compounds are more stable than true hydrates; thus they do not lose water in the vacuum desiccator.

Allied to this power of forming loose compounds may be the remarkable power possessed by most solids of retaining a film of water adsorbed on the surface. Almost any powder which has stood exposed to the air loses water when heated. Glass obstinately retains water both on the surface and actually within the surface layer.

**209. Efflorescence and Deliquescence.**—Certain substances become moist in presence of air and finally liquefy. These are said to be *deliquescent*. Deliquescence occurs if the saturated solution of the salt has a lower vapour pressure than the partial pressure of water vapour prevailing in the atmosphere. Water condenses on the salt and the saturated solution formed from it, and the whole gradually liquefies.

The hydrates themselves have a certain definite vapour pressure, and if this is greater than the partial pressure of water vapour in the air, water will leave the salt and pass into the atmosphere. The crystals of the salt fall to powder and it is said to be *efflorescent*. Thus the ordinary hydrate of sodium carbonate, $Na_2CO_3 . 10H_2O$, has a vapour pressure of 24·2 mm. The partial pressure of water vapour in the air is 10–20 mm. Accordingly, this salt loses water and effloresces.

**210. Detection and Estimation of Water.**—Water is recognised when pure by its physical constants (density = 1, B.P. 100° C., F.P. 0° C.), but the use of these presupposes the possibility of the obtaining of pure water in quantities of about ½ c.c. at least. Traces of water vapour may be detected and estimated by passing the gas suspected of containing them over weighed phosphorus pentoxide. Traces of water contained in organic liquids may be detected by adding white anhydrous copper sulphate, which is turned to the blue pentahydrate by the action of water. Water dissolved in another liquid may be estimated by adding calcium carbide and measuring the volume of acetylene evolved according to the equation

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

Water adherent to or loosely combined with non-volatile solids is estimated by drying the weighed solid in the desiccator, steam oven or air oven till its weight is constant, the loss of weight repre-. senting the water present.

## HYDROGEN PEROXIDE

**211. Hydrogen Peroxide. Formation and Preparation.**—Hydrogen peroxide is formed in small quantities when hydrogen and oxygen combine. Thus the water obtained by condensation, when a hydrogen flame impinges on water, contains traces of the substance.

It appears that the reaction of hydrogen and oxygen takes place at certain temperatures by a chain of reactions :—

$$H_2 + O_2 = H_2O_2, \quad (1)$$

$$H_2O_2 + H_2 = 2H_2O^*,^1 \quad (2)$$

$$2H_2O^* + 2O_2 = 2O_2^* + 2H_2O, \quad (3)$$

$$2O_2^* + 2H_2 = 2H_2O_2, \quad (4)$$

in which the hydrogen peroxide is an essential linkage. The condensed water then naturally contains traces of this intermediate product.

Hydrogen peroxide is ordinarily made by the reaction of certain peroxides with water or acids.

Thus, when sodium peroxide (§ 226) is added to an excess of ice-cold water, sodium hydroxide and hydrogen peroxide are formed,

$$Na_2O_2 + 2H_2O = 2NaOH + H_2O_2.$$

It is not easy to separate hydrogen peroxide from soluble salts formed at the same time, and accordingly the peroxide of barium,

[1] The asterisk attached to the symbol of a molecule indicates that it is *activated*, *i.e.*, carries with it some or all of the energy of the chemical reaction producing it, and has therefore greater chemical activity than the non-activated molecules.

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which has an insoluble sulphate and carbonate, is the usual starting point. Thus barium peroxide may be added to water through which a stream of carbon dioxide is passing,

$$BaO_2 + H_2CO_3 = BaCO_3 + H_2O_2,$$

and the insoluble carbonates removed by filtration. The following method is commonly used.

Twenty cubic centimetres of concentrated sulphuric acid are

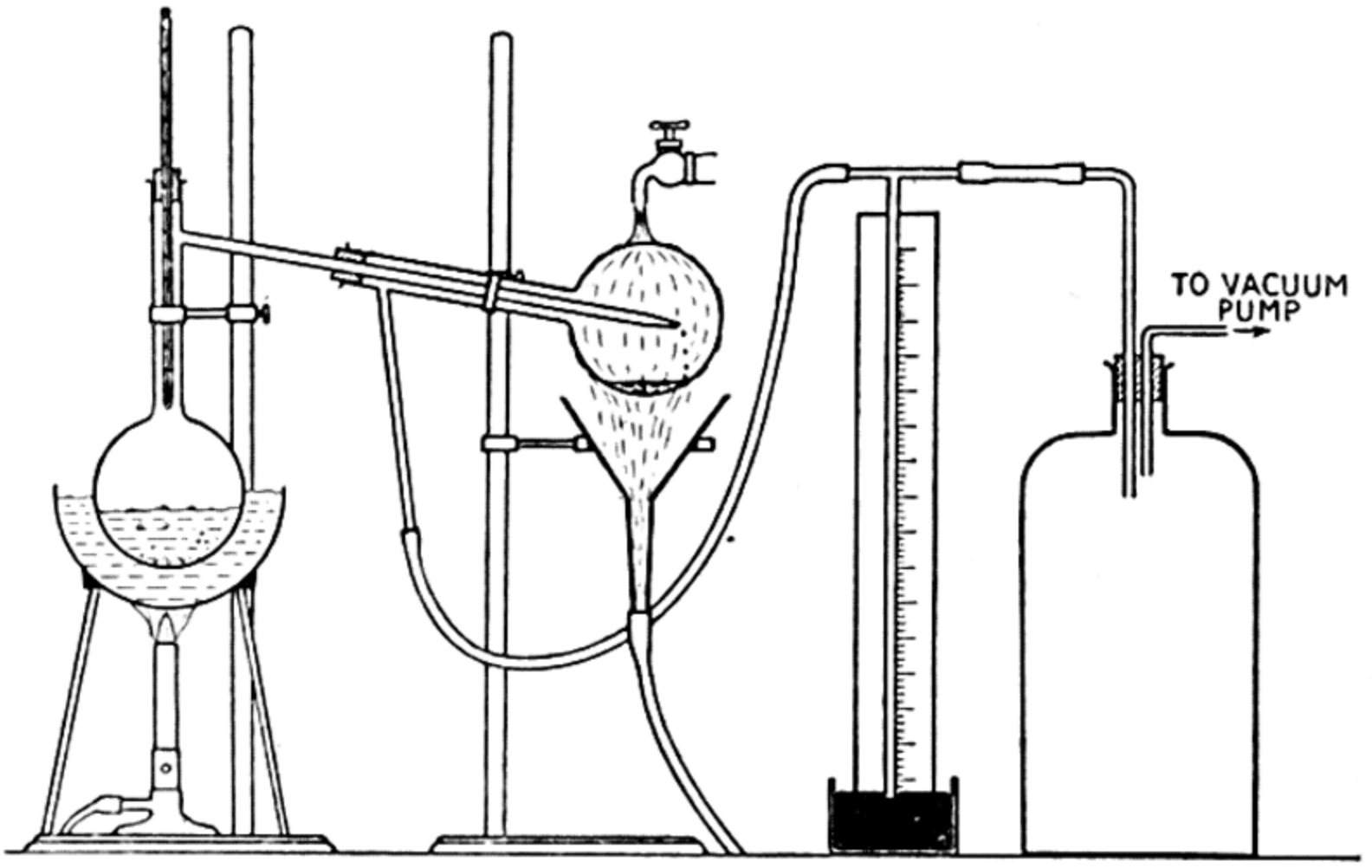


FIG. 71.—Distillation of hydrogen peroxide under reduced pressure.

diluted with 200 c.c. of water and cooled to near 0° C. by means of a freezing mixture. Into this solution are stirred small portions of hydrated barium peroxide ground to a thin cream with water, and this is continued until the solution is only just acid. The solution is allowed to stand in the ice chest for some twenty-four hours. The insoluble barium sulphate formed by the reaction,

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2,$$

settles out and the solution is then filtered. The excess of sulphuric acid is then exactly neutralised with a few drops of barium hydroxide and again filtered, leaving a pure

$$Ba(OH)_2 + H_2SO_4 = BaSO_4 \downarrow + 2H_2O$$

solution of hydrogen peroxide. The success of the preparation depends mainly on good cooling, good stirring, and never having an excess of barium peroxide, for this reacts with the hydrogen peroxide formed.

Hydrogen peroxide is prepared industrially by the electrolysis of ice-cold 50% sulphuric acid, yielding persulphuric acid (§ 946).

This is hydrolysed by steam and the hydrogen peroxide is distilled off and fractionated under reduced pressure,

$$2HSO_4^- = H_2S_2O_8 + 2\ominus$$
$$H_2S_2O_8 + 2H_2O = 2H_2SO_4 + H_2O_2.$$

In this process no materials other than water and energy are used up.

If pure anhydrous hydrogen peroxide is required, the solution may be evaporated at a temperature of 60–70° C. until it contains some 45 per cent. of hydrogen peroxide. Further evaporation merely causes decomposition to water and oxygen. To prepare 100 per cent. hydrogen peroxide the solution may be distilled under reduced pressure (*c.* 15 mm.). The strong solution is placed in a flask and heated to 35–40° C. under a pressure of 15 mm. The liquid distilling over is mainly water. When the temperature of the contents of the flask has risen to about 70° C. the process is stopped. The liquid remaining in the flask is hydrogen peroxide containing only a small proportion of water. By distilling this or by evaporating it in a vacuum desiccator over sulphuric acid or by cooling it till crystals of pure hydrogen peroxide separate, 100 per cent. pure hydrogen peroxide can be obtained.

Hydrogen peroxide is produced in some quantity when certain substances are oxidised in presence of water. Thus, if turpentine is oxidised by air in the presence of water, as much as 0·5 per cent. of hydrogen peroxide may be formed. The well-known disinfectant, Sanitas, owes some of its efficacy to the presence of hydrogen peroxide formed in this way.

**212. Formula of Hydrogen Peroxide.**—When the pure peroxide is decomposed 1 gram-molecule of oxygen is formed for every 2 gram-molecules of water. The formula must accordingly be $(HO)_n$,

$$4(HO)_n = 2nH_2O + nO_2.$$

The freezing-point of its solutions (§ 60) indicates a molecular weight of 34. The formula must therefore be $H_2O_2$.

**213. Physical Properties.**—Pure anhydrous hydrogen peroxide is a colourless or very faintly blue liquid of a syrupy consistency. It is odourless. The dilute solutions have a metallic taste; the pure substance corrodes and blisters the skin. It boils at 84·85° C. at 68 mm. pressure.

**214. Chemical Properties.**—*Decomposition.*—Hydrogen peroxide is readily decomposed when heated to temperatures of near 100° C., water and oxygen being formed,

$$2H_2O_2 = 2H_2O + O_2.$$

The pure substance may decompose explosively. The decomposi-

tion is greatly accelerated by numerous catalysts, of which the finely divided noble metals, gold, platinum and silver, are the most effective. Carbon, iodine and many oxides have the same effect. Certain organic substances also catalyse the decomposition of hydrogen peroxide. The enzyme known as blood-catalase, which is present in blood, does this very effectively, and a drop of blood, allowed to fall into hydrogen peroxide, causes a brisk evolution of oxygen. The strength of hydrogen peroxide solutions is expressed in terms of the number of volumes of oxygen they produce on decomposition. Thus the solution of hydrogen peroxide sold as of 10-volume strength evolves ten times its volume of oxygen when heated until completely decomposed. It is easily calculated that it contains about 3 per cent. of hydrogen peroxide ; 10-volume, 20-volume and 100-volume hydrogen peroxide are articles of commerce.

Hydrogen peroxide has weak acidic properties. Thus, when added to barium hydroxide or potassium hydroxide the corresponding peroxide is formed,

$$Ba(OH)_2 + H_2O_2 + 6H_2O = BaO_2.8H_2O.$$

*Oxidising Action.*—Hydrogen peroxide is a powerful oxidising agent, reacting with a reducing agent $X$, according to the equation,

$$nH_2O_2 + X = nH_2O + XO_n.$$

Among these reactions we may mention the following :—

Arsenites are oxidised to arsenates (§ 800) ; sulphides, sulphites and thiosulphates to sulphates (§§ 917, 924) ; ferrous compounds to ferric compounds, alkaline suspensions of chromic hydroxide to chromates (§ 984), iodides to iodine (§ 1095). It oxidises numerous organic substances, particularly in presence of ferrous sulphate, which acts as a catalyst.

In consequence of this powerful oxidising action hydrogen peroxide bleaches numerous organic colouring matters. Dark hair is lightened in tone by hydrogen peroxide and the ' peroxide blonde ' owes her golden hair to the use of this substance. It finds numerous applications for bleaching other delicate substances, *e.g.*, ostrich feathers, ivory, silk, etc. Its oxidising action on sulphides is utilised in the restoration of pictures. The darkening of these is due to white lead carbonate being converted into brown-black lead sulphide. Hydrogen peroxide oxidises this to the white lead sulphate.

The oxidising action of hydrogen peroxide makes it a useful agent for cleansing wounds. Though not a very powerful destroyer of bacterial life, it has the power of dissolving and oxidising the coagulated blood, pus, etc., in which the bacteria find a breeding ground.

*Deoxidising Action.*—Hydrogen peroxide reacts with many powerful oxidising agents in such a way that both it and the oxidising

agent are reduced. In general, a powerful oxidising agent, $XO_n$, reacts with hydrogen peroxide, thus

$$XO_n + nH_2O_2 = X + nO_2 + nH_2O.$$

Thus hydrogen peroxide reacts with silver oxide, forming silver, oxygen and water,

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

The peroxides of manganese and lead, in presence of acids, form their lower salts and oxygen,

$$2HCl + PbO_2 + H_2O_2 = PbCl_2 + 2H_2O + O_2.$$

Acid solutions of permanganates are reduced to manganous salts with evolution of much oxygen (§ 861 (7) ):

$$5H_2O_2 + 2KMnO_4 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

This reaction is used for the volumetric estimation of hydrogen peroxide, and also for the preparation of oxygen.

The reaction of hydrogen peroxide with dichromates is complex in character and is discussed under the heading of the latter salts. In acid solution a deep blue solution is formed, probably containing chromium peroxide, $CrO_5$ (§ 995). This is unstable in aqueous solution and decomposes within a few seconds, giving green chromic salts and oxygen (§ 995) ; it is, however, soluble in ether, and in ethereal solution is fairly permanent. This reaction affords a delicate test for hydrogen peroxide.

**215. Tests for Hydrogen Peroxide.**—Hydrogen peroxide is the only substance which will liberate iodine from potassium iodide in presence of ferrous sulphate. Thus, to test for the substance we may add the suspected liquid to an acidified solution of potassium iodide mixed with a little ferrous sulphate and starch. A blue colour indicates the liberation of iodine and the consequent presence of hydrogen peroxide,

$$H_2O_2 + 2HI = 2H_2O + I_2.$$

The dichromate test is very distinctive. A layer of ether is poured on to the surface of a cold acid solution of potassium dichromate. The suspected liquid is added and the mixture is shaken. If hydrogen peroxide is present the ether is coloured blue (see above and § 995).

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# CHAPTER X

## THE ALKALI METALS AND THEIR COMPOUNDS

**216. Group I. A. of the Periodic Table.**—Group I. A. of the periodic table is usually taken as consisting of the elements hydrogen, lithium, sodium, potassium, rubidium, cæsium and francium. Hydrogen is, however, hardly to be classified in any group of the periodic table. It certainly resembles these elements in being strongly electro-positive and monovalent, but is, from the chemical point of view, best considered separately (§ 177). The radioactive element francium has not been isolated in quantities that would allow of chemical investigation.

The remaining elements show a remarkable likeness and a steady gradation of properties with increasing atomic weight.

The metals themselves are soft, very fusible and volatile, and their vapours give strong characteristic colours to the Bunsen flame.

The elements are extremely reactive, lithium least so and cæsium most. Their oxides are strongly basic and react with water, forming soluble hydroxides—the caustic alkalis. The alkali metals have very few insoluble salts. Thus their carbonates, sulphides, and other salts of weak acids, are soluble and form strongly alkaline solutions (§ 121).

The salts of the alkali metals are of greater stability than those of other metals. Their carbonates and hydroxides are not decomposed at a red heat. Their nitrates, too, do not decompose to oxides of nitrogen, oxygen and the metallic oxide, but only to the nitrite and oxygen. They are also the only metals which form bicarbonates which are stable in the solid state.

The salts of potassium and sodium play an important part both in pure and applied chemistry. In processes where the salt of a particular acid is required, the sodium or potassium salt, other things being equal, is normally used for several reasons.

Almost all sodium and potassium salts are soluble in water, and in many cases the salts of these metals and of ammonium are the only available soluble salts. Thus the carbonates, hydroxides, phosphates and silicates of the alkali metals are soluble, while those of other metals are not.

Again, the soluble salts of many other metals cannot be used in neutral or alkaline solution without precipitating a basic salt or the hydroxide, which might contaminate the substance prepared.

Finally, on account of the extreme abundance of common salt in a state of comparative purity the cost of sodium salts is lower than that of the salts of any other element, calcium possibly excepted, and, accordingly, other things being equal, sodium salts are preferred for industrial purposes.

### Lithium Li, 6·94

The element lithium is interesting on account of its very low atomic weight and simple atomic structure (§ 146[2]). It finds, however, few uses either in scientific or industrial work.

**217. Occurrence.**—The chief compounds of lithium are various silicates, such as *lepidolite*, which contains lithium aluminium fluosilicate; and *spodumene*: lithium aluminium silicate. The element is widely distributed, being found in traces in the ashes of many plants. It also occurs in certain mineral springs.

**218. Preparation.**—Many processes for the extraction of lithium from its ores have been devised. In one of these the powdered silicates (*e.g.*, lepidolite) are fused with excess of barium carbonate, barium sulphate and potassium sulphate at a high temperature. Two layers are formed, the lower of silicates. of barium, aluminium, etc., and the upper of lithium and potassium sulphates. The latter layer is dissolved in water and converted into chlorides by the action of barium chloride solution. The solution is evaporated and the lithium chloride extracted with alcohol and ether, in which potassium and sodium chlorides do not dissolve.

The metal is made by the electrolysis of fused lithium chloride, using a carbon anode and iron cathode.

**219. Properties.**—Lithium is a white metal softer than lead but harder than the other alkali metals. It fuses at 186° C. The metal is fairly volatile and the vapour gives to the Bunsen flame a carmine red colour, occasioned by bright red and weaker orange spectral lines. It has a density of 0·534, lower than that of any element solid at ordinary temperatures. Its specific heat, 0·9408, is higher than that of any other element.

Lithium is the least reactive of the alkali metals, but is none the less strongly reactive. It burns at 200° C. to lithium monoxide, a little peroxide being also formed,

$$4Li + O_2 = 2Li_2O.$$

It forms a nitride very readily and combines with the halogens, sulphur and hydrogen.

Lithium reacts with water, forming lithium hydroxide LiOH and hydrogen. Unlike potassium and sodium it neither fuses nor burns when thrown into water. Lithium, of course, reacts very readily with all acids.

**220. Lithium Compounds** in general resemble those of sodium, the chief differences noticeable being the small solubility of the carbonate, fluoride and phosphate. In these and certain other respects lithium shows some resemblance to magnesium and the alkaline earth metals, notably in the solubilities of its salts. Its salts, unlike those of the other alkali-metals, are almost all hydrated.

It may be noted that the element at the head of each of the earlier groups

of the periodic table tends to resemble the element one period below it in the next higher group. Thus we see the following resemblances in addition to those indicated by the normal grouping of the periodic table.

| Group I. | Group II. | Group III. | Group IV. |
|---|---|---|---|
| Li | Be | B | C |
| Na | Mg | Al | Si |
| K | Ca | Sc | |

The reason of this phenomenon is that the ions become larger as we go down the periodic table, and thus the density of the electric field surrounding the ions decreases with increasing atomic weight in any given group. But passing from left to right across the table, the valency, and hence the charge, increases; thus leading to the observed diagonal relationships, for the increased charge on the ion of heavier weight in the higher group is largely compensated by the increased size, leading to a similar density of surface electric field. As this field strength determines many properties of ions, those with similar surface field densities resemble each other in their properties.

*The atomic weight* of lithium was determined by a method similar to that used for sodium (§ 225), and 6·94 is the most reliable value.

Lithium oxide $Li_2O$ can be made by heating the metal in air or, better, by heating the hydroxide to redness,

$$2LiOH = Li_2O + H_2O.$$

Lithium oxide resembles sodium oxide except in that its reaction with water is slow,

$$Li_2O + H_2O = 2LiOH.$$

*Lithium peroxide* is made by the action of hydrogen peroxide on lithium hydroxide,

$$2LiOH + 2H_2O_2 + H_2O = Li_2O_2 . H_2O_2 . 3H_2O.$$

A double compound with hydrogen peroxide is precipitated, and is carefully dried over phosphorus pentoxide. A true peroxide $Li_2O_2$ has now been prepared.

*Lithium hydroxide* LiOH is made by the action of water on the metal,

$$2Li + 2H_2O = 2LiOH + H_2.$$

The action is not violent. It is a white crystalline substance resembling caustic soda but much less soluble in water.

*Lithium carbonate* $Li_2CO_3$ is prepared by the action of ammonium carbonate on a lithium salt. The carbonate crystallises out, being sparingly soluble,

$$Li_2SO_4 + (NH_4)_2CO_3 = Li_2CO_3 + (NH_4)_2SO_4.$$

It is a white solid, sparingly soluble in water (1·54 gms. per 100 gms. water at 0° C., and only 0·72 gm. per 100 gms. water at 100° C.).

It resembles sodium carbonate except in so far that it is decomposed to the oxide when heated to strong redness. The bicarbonate, like that of magnesium, is stable in solution only.

*Lithium orthophosphate* is practically insoluble in water (0·03 per cent. at 25° C.). Its precipitation, when sodium phosphate is added to a lithium salt, is used in analysis to distinguish the latter from the salts of the other alkali metals.

*Lithium sulphate* $Li_2SO_4$ crystallises with only one molecule of water of crystallisation. It is soluble in water.

*Lithium fluoride* LiF is sparingly soluble (0·27 parts in 100 parts water at 18° C.).

*Lithium chloride* LiCl in its general behaviour resembles sodium chloride. It is, however, deliquescent and very much more soluble in water.

**221. Detection and Estimation of Lithium Compounds.**—Lithium is detected by the red coloration it gives to the Bunsen flame and by its spectrum. The addition of sodium phosphate to solutions of lithium salts precipitates lithium phosphate (p. 255).

Lithium is sometimes estimated by precipitation as the latter salt.

## SODIUM Na, 22·997

**222. History.**—Sodium chloride (common salt), and sodium carbonate have been known from the earliest times. The first is a necessity of life and is known to most primitive peoples. Native sodium carbonate was known to the Egyptians and used in embalming. The words translated as " nitre " in the Bible represent sodium carbonate, as is shown in the two passages :—

"For though thou wash thee with nitre, and take thee much soap . . ." —*Jer. ii.* 22.

"As he that taketh away a garment in cold weather, and as vinegar upon nitre, so is he that singeth songs to an heavy heart."—*Prov. xxv.* 20.

The allusion to the effervescence produced when acetic acid acts on sodium carbonate is probably the earliest reference to the reactions of an acid. Borax, sodium diborate, has been known

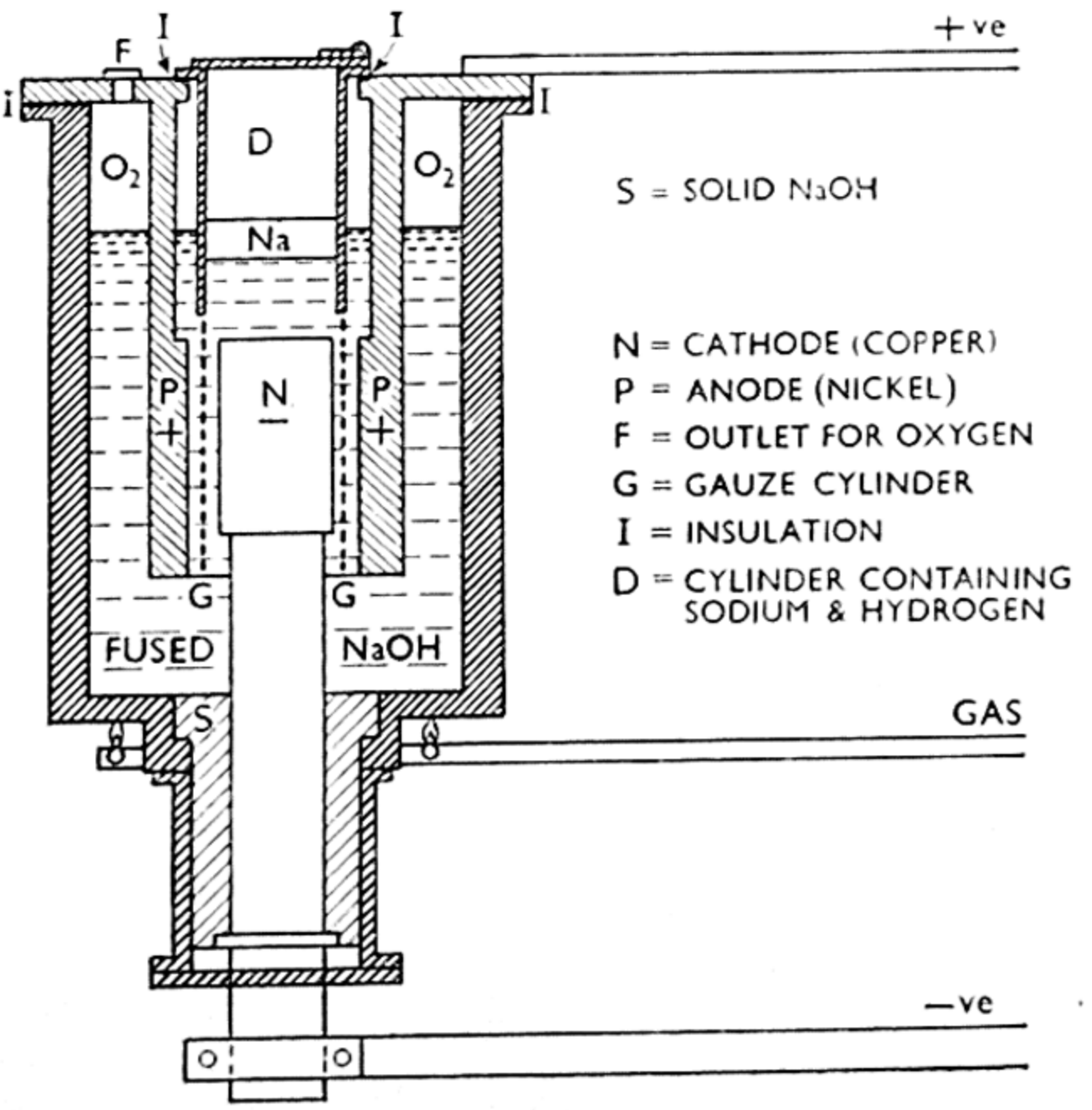


FIG. 72.—Castner process for manufacture of sodium.

since about the eighth century A.D. Caustic soda was distinguished from caustic potash in the eighteenth century.

The metal sodium was first isolated by Sir Humphry Davy in 1807, by the electrolysis of fused caustic soda.

**223. Preparation of Metallic Sodium.**—Sodium can be made by the reduction of sodium peroxide with carbon,

$$3Na_2O_2 + 2C = 2Na_2CO_3 + 2Na,$$

and also by reduction of caustic soda with magnesium, but commercially the electrolysis of caustic soda or sodium chloride is employed.

In the Castner process fused caustic soda is contained in an iron vessel heated by gas jets. The copper negative electrode N passes up through the base and is sealed in position by solid caustic soda. The end of the electrode is surrounded by steel wire gauze, above which is a cylinder D. The positive electrode P surrounds this cylinder. When electrolysis occurs the caustic soda decomposes,

$$NaOH = Na + OH.$$

The sodium collects at the negative electrode and rises into the cylinder D, whence it is removed from time to time by ladles. The hydroxyl at the positive electrode forms water and oxygen,

$$4OH = O_2 + 2H_2O,$$

which latter gas escapes from an exit hole. The water dissolves in

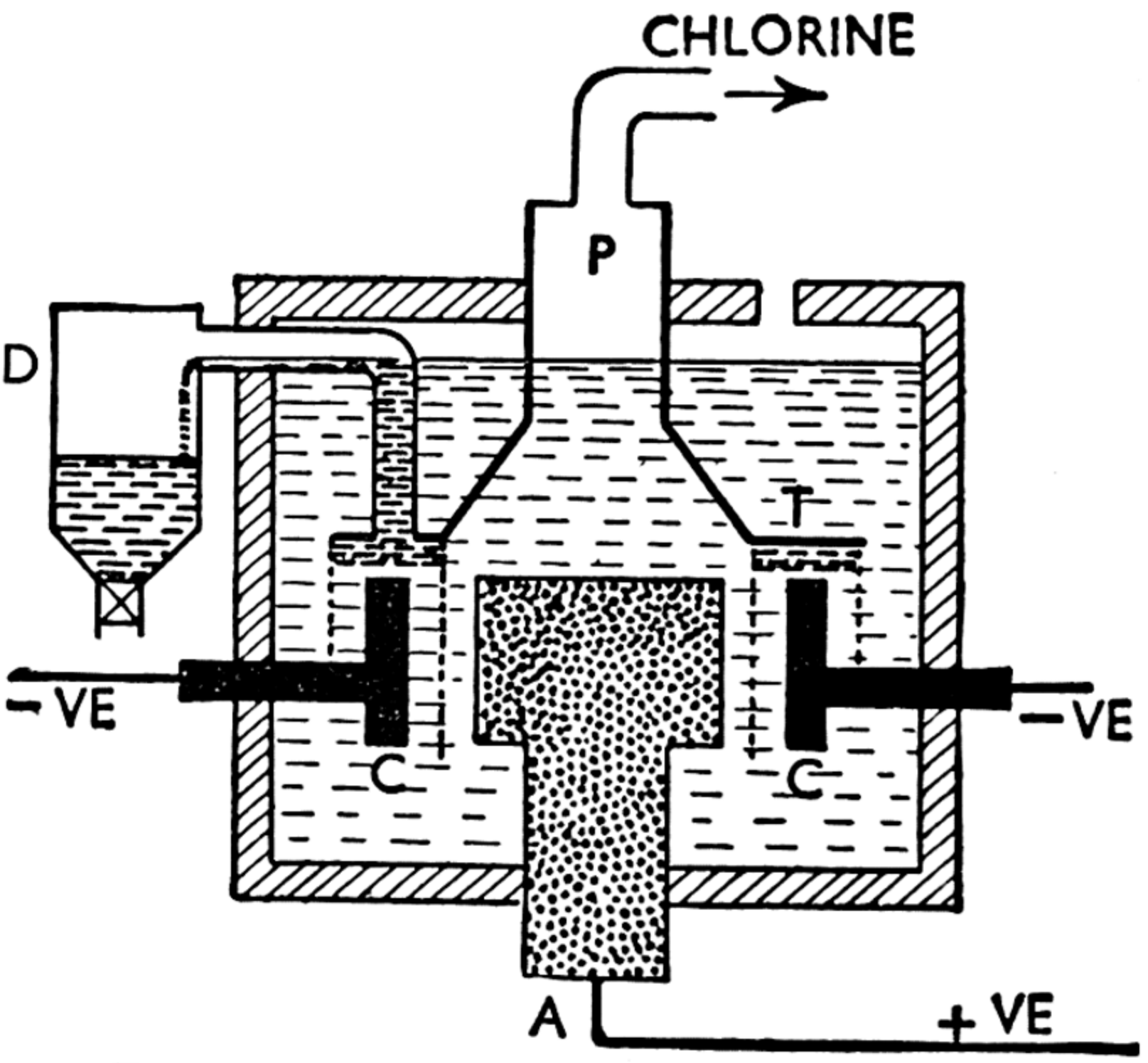


FIG. 72A.—Downs cells for manufacture of sodium.

the melted caustic soda and in consequence a good deal of hydrogen is formed and escapes by a second exit pipe provided above the cylinder D.

The efficiency of the Castner process is not very high, and the electrolysis of fused sodium chloride is now a favoured method in the U.S.A. and Germany. The Downs cell is shown in Fig. 72A. The electrolyte is a mixture of fused sodium chloride with potassium chloride and fluoride. This mixture is fluid at 600° C., whereas pure sodium chloride fuses about 800° C., which is above the boiling point of metallic sodium. The chlorine is formed at the carbon anode A and escapes through the pipe P. The sodium rises from the cathode C into the ring-shaped inverted trough T whence it is forced by the pressure of the fused sodium chloride into the receptacle D. The efficiency is about 70 per cent., higher than that of the Castner cell.

**224. Properties.**—Sodium is a white lustrous metal. As usually seen it is coated with hydroxide, but a freshly cut surface is silvery white. The metal is very soft; it can be cut with a knife, and at ordinary temperatures can be moulded with the dry fingers. It is lighter than water (D = 0·97). Sodium melts at 97·5° C. and boils at 784·2° C. Its vapour is monatomic, but contains a small proportion of $Na_2$ molecules. Its specific heat is 0·28 at 0° C. The metal is a very good conductor of electricity.

Sodium reacts with oxygen, burning readily in air, forming sodium oxide and peroxide.

$$4Na + O_2 = 2Na_2O$$
$$2Na + O_2 = Na_2O_2.$$

The flame has a brilliant yellow colour. The spectrum of sodium shows the famous D lines in the yellow, which are used as the standard of wavelength in spectroscopy. It burns when heated with the halogens, phosphorus and sulphur, forming the halides NaCl, NaBr, etc., the phosphide $Na_3P$, and various sulphides (*q.v.*). Sodium combines also with hydrogen at 360°, forming a rather unstable hydride, NaH (§ 190).

Sodium reacts with the majority of *oxides*. Thus it decomposes water energetically, forming sodium hydroxide and hydrogen,

$$2Na + 2H_2O = 2NaOH + H_2.$$

The metal melts and travels as a globule over the surface of the water. The hydrogen does not catch alight unless large pieces of sodium are used, when dangerous explosions may result. If the sodium is restrained from moving, as, for example, by placing it on wet blotting paper, the hydrogen ignites and burns with the brilliant yellow sodium flame. Care should always be exercised, as even small pieces of the metal may explode unaccountably.

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When sodium is heated with the oxides or chlorides of most of the metals it reduces them to the metal. The method has been used to prepare beryllium, titanium, uranium and other metals (§ 653),

$$2Na + BeCl_2 = 2NaCl + Be.$$

The method is sometimes of practical value, but the aluminothermic method is usually more convenient for the preparation of these elements. Sodium reacts with ammonia gas, giving sodamide (§ 242),

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

Sodium amalgam is discussed in § 437. It contains compounds of sodium and mercury. It reacts with water much less vigorously than sodium itself and forms a very convenient alkaline reducing agent.

*Uses of Sodium.*—Sodium is employed in the manufacture of sodium peroxide (§ 226), sodium cyanide (§ 241) and sodamide. About half of the sodium made is used in the manufacture of the 'anti-knock,' lead tetra-ethyl. It finds a considerable use as a reagent in organic chemistry.

**225. Atomic Weight of Sodium.**—The best method of determining the equivalent of sodium is that of Richards and Wells, who precipitated a known weight of sodium chloride with silver nitrate. There is abundant evidence that the alkali metals are univalent, such as the molecular weight of the chlorides in solution, which indicates formulæ XCl, etc. We may, accordingly, regard sodium chloride as having the formula NaCl. Richards and Wells found that the ratio NaCl : AgCl was 40·7797 : 100 and arrived at the value of 23·008 for the atomic weight of sodium. Taken in conjunction with other determinations the value 22·997 is the most probable. Aston finds that there are no isotopes of sodium.

**226. Sodium Oxides.**—There are two oxides of sodium :—

Sodium monoxide, $Na_2O$.
Sodium peroxide, $Na_2O_2$.

*Sodium monoxide* $Na_2O$ is rarely met with. It is formed by the combustion of sodium, or better by heating sodium azide with sodium nitrite or nitrate in a nickel crucible,

$$3NaN_3 + NaNO_2 = 2Na_2O + 5N_2.$$

Sodium monoxide is a white solid. It combines vigorously with water, forming the hydroxide,

$$Na_2O + H_2O = 2NaOH.$$

*Sodium Peroxide* $Na_2O_2$.—This substance is prepared by passing a plentiful supply of dry air over burning sodium contained in aluminium trays.

$$2Na + O_2 = Na_2O_2.$$

It forms a yellowish powder. Unlike most peroxides, it is not decomposed by heat. It is a most valuable oxidising agent and finds numerous uses in laboratory work.

With water or acids it yields hydrogen peroxide and also some free oxygen, especially when the peroxide is in excess and the temperature is allowed to rise :

$$Na_2O_2 + 2H_2O \rightleftharpoons 2NaOH + H_2O_2$$
$$2Na_2O_2 + 2H_2O = 4NaOH + O_2,$$
$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2.$$

The reaction with water is reversible, for when hydrogen peroxide is mixed with cold concentrated caustic soda solution, hydrated sodium peroxide $Na_2O_2 \cdot 8H_2O$ crystallises out.

Sodium peroxide oxidises carbon monoxide, forming sodium carbonate,

$$Na_2O_2 + CO = Na_2CO_3.$$

Carbon dioxide is absorbed, oxygen being liberated,

$$2Na_2O_2 + 2CO_2 = 2Na_2CO_3 + O_2.$$

Thus sodium peroxide has been used partially to restore air which has been breathed to its original condition.

Sodium peroxide oxidises ammonia to nitrogen, oxides of nitrogen to nitrates, and sulphides to sulphates.

The sulphur in an insoluble sulphide, such as iron pyrites, may be determined by fusing the mineral with sodium peroxide, so converting the sulphur into sodium sulphate, which is readily determined by precipitation with barium chloride,

$$15Na_2O_2 + 2FeS_2 = 4Na_2SO_4 + Fe_2O_3 + 11Na_2O.$$

### Sodium Hydroxide, Caustic Soda, NaOH

**227. Preparation of Sodium Hydroxide.**—Sodium hydroxide is prepared by three methods :—

(1) The action of sodium on water.

(2) The action of calcium hydroxide on sodium carbonate.

(3) The electrolysis of sodium chloride solutions.

The first method is used to obtain very pure caustic soda for laboratory purposes. The second is a well-known commercial process (which may be applied experimentally in the laboratory). The third is the chief modern commercial method of making caustic soda.

**228. Laboratory Preparation of Pure Caustic Soda.**—Very pure caustic soda solution, free from carbonate, which is required for certain titrations, etc., may be made in the laboratory by the action of the metal on water.

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Distilled water is boiled for twenty minutes to remove carbon dioxide and placed in an Erlenmeyer flask to cool, carbon dioxide being excluded by a soda-lime guard tube. A layer of ether, 3–4 cm. deep, is then floated on the water and bits of clean metallic sodium of the size of a bean or smaller are added. The sodium sinks but remains in the ether layer, where it reacts with dissolved water, the caustic soda formed passing into the watery layer,

$$2Na + 2H_2O = 2NaOH + H_2.$$

There is no danger as long as the ether layer is thick enough to prevent the sodium coming into contact with both air and water. The bulk of the ether is removed with a pipette and the rest by boiling (with precautions to avoid ignition of ether vapour !). Caustic soda solution so prepared contains no carbonate.

Crude caustic soda may be purified by dissolving it in alcohol, in which liquid the impurities are not soluble. The solution is decanted or filtered from these and evaporated in a silver dish.

**229. Preparation of Sodium Hydroxide from Sodium Carbonate.**—This method is based on the principle of double decomposition. Calcium hydroxide, slaked lime, is soluble in water to the extent of about 1 part in 250 of water, while calcium carbonate is almost insoluble. When a solution of sodium carbonate and a solution of calcium hydroxide are mixed, sodium hydroxide and calcium carbonate are formed,

$$Ca(OH)_2 + Na_2CO_3 \rightleftharpoons CaCO_3 \downarrow + 2NaOH.$$

In practice even a saturated solution of slaked lime is so dilute that the sodium carbonate solution is mixed with solid calcium hydroxide. The latter gradually dissolves and reacts with the sodium carbonate in the manner indicated above. In the laboratory the procedure indicated below may be followed.

Dissolve 20 gms. of sodium carbonate in 200 c.c. of water in an iron (or porcelain) dish, and heat to boiling. Add gradually over half an hour, 25 gms. of slaked lime, stirring at short intervals. Remove the source of heat ; allow the precipitate to settle, pour off the clear liquor and evaporate in an iron or silver dish until the fused sodium hydroxide remaining solidifies on cooling.

This was formerly the only method for the manufacture of caustic soda and still accounts for a third of the total production.

Some form of crude sodium carbonate solution, either the solution made by lixiviating the black-ash of the Leblanc process (§ 235) or a solution of the soda-ash obtained by the ammonia-soda process (§ 236), is heated and agitated with slaked lime, made by immersing lumps of quicklime in the liquor. After settling, the clear solution of caustic soda is run off from the sediment of calcium carbonate, evaporated considerably in iron pots, and then allowed to cool. Sodium carbonate, sulphate, etc., crystallise out and the remaining liquid is then evaporated till steam ceases to be evolved. The liquid, consisting of melted caustic soda, is run off into iron drums.

**230. Preparation of Caustic Soda by Electrolytic Methods.**—The principle of this process is indicated in Chapter VI. When an electric current is passed through a solution of sodium chloride, sodium hydroxide is produced at the cathode and chlorine at the anode (see §§ 203, 162). The practical difficulty of the process lies in the separation of the caustic soda from the sodium chloride present.

Two chief types of cell are used in making caustic soda by the electrolysis of sodium chloride.

(1) Cells in which the anode and cathode are separated by a porous diaphragm.

(2) Cells using a mercury cathode.

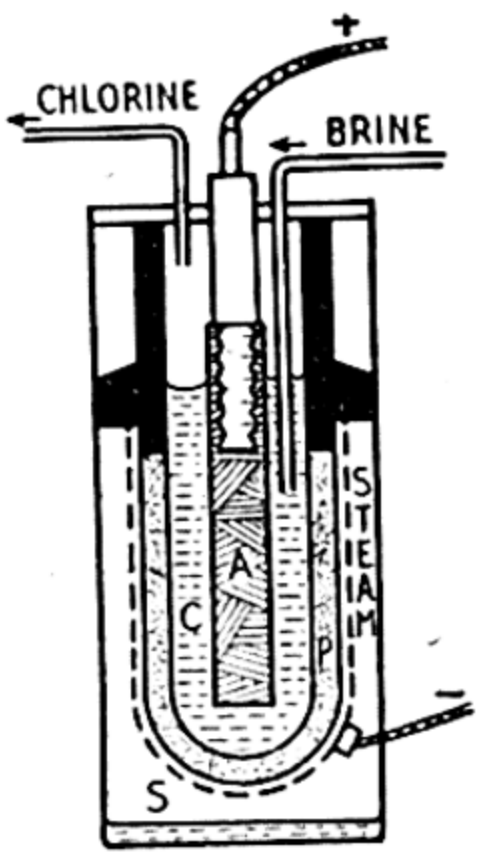


FIG. 73.—Nelson electrolytic cell for caustic soda.

(1) *Diaphragm Cells.*—The most important of these is probably the *Nelson* cell, a modification of the Hargreaves-Bird pattern. Several other patterns are used but are not very different in principle.

An inner U-shaped cell C, with a wall of porous asbestos, contains a graphite anode A, connected to the positive electrical supply. The porous asbestos diaphragm (P) is directly in contact with the perforated steel cathode S, connected to the negative main. Brine runs into the cell C, and is kept at a constant level by an automatic arrangement. It percolates by gravity through the asbestos diaphragm and is electrolysed while doing so.

Chloride ions travel to the anode A and are discharged, forming gaseous chlorine. The sodium ions travel to the cathode, where at the same time hydrions are discharged and are replaced by further ionisation of the water. The hydroxyl ions formed at the same time, together with the sodium ions and some water, percolate through the perforated steel cathode S, and are, of course, a solution of caustic soda. This solution passes away along the bottom of the outer casing. The outer casing is kept full of steam, which heats the liquor and reduces its resistance, and also promotes the removal of the caustic soda from the pores of the diaphragm. The liquor so obtained is evaporated and caustic soda is obtained. The caustic soda is apt to contain some undecomposed chloride. The cells have a very high efficiency, *i.e.*, turn about 90 per cent. of the electrical energy of the current passing into chemical energy.

The drawing (Fig. 73) is a section. In fact, the cell contains up to twenty anodes in line and has the form of a long U-shaped trough.

(2) *Mercury Cathode Cells.*—Cells of these patterns produce caustic soda of very high purity, but at a greater cost than that

*Sodium Chloride Solution.*

$2Na^+$ + $2Cl^-$

$2H_2O \rightleftarrows H^+ + 2OH^-$

$H^+ \rightarrow H_2\uparrow$ ; $2Cl^- \rightarrow Cl_2\uparrow$

Cathode. Anode.

$2Na^+ + 2OH^-$

Sodium hydroxide solution.

involved in the use of the diaphragm cells, for, though using current very efficiently, great quantities of mercury are required. Thus a plant utilising 6,000 h.p. requires about 72 tons of mercury which, although not used up, represent a capital value which causes an appreciable addition to the cost of the material made.

The modern type of cell (Fig. 74) has a number of carbon anodes and a cathode consisting of a stream of mercury flowing continuously along the bottom of the cell. Brine flows slowly through the cell. Electrolysis takes place. Chlorine is evolved at the carbon anodes, while free sodium is liberated at the mercury cathode and dissolves in mercury. The mercury leaving the cell and containing dissolved sodium flows into a trough through which water is circulated; the sodium reacts with the water, giving sodium hydroxide and hydrogen,

$$2Na + 2H_2O = 2NaOH + H_2.$$

The solution of sodium hydroxide is concentrated and allowed to

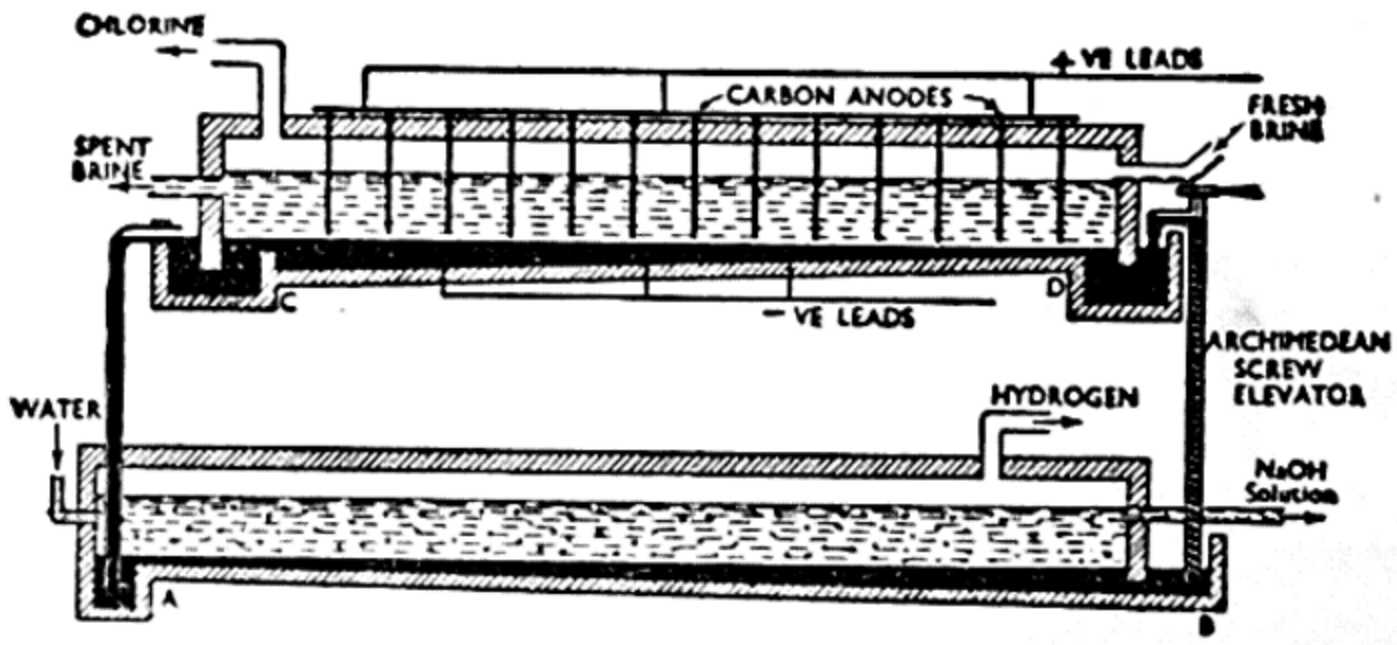


FIG. 74.

solidify. The mercury freed from sodium is returned to the electrolytic cell.

**231. Properties of Sodium Hydroxide.**—Sodium hydroxide is a white solid. It is usually sold as sticks or powder. It has, in weak solution, the characteristic soapy taste and feel of an alkali. Strong solutions and the solid are very corrosive, attacking and dissolving the skin, or, if swallowed, damaging the membranes of the throat and stomach. Care should therefore be taken in sucking up sodium hydroxide solution with the pipette, for fatalities have occurred through the liquid being swallowed. The name, "caustic" soda, was given to the substance on account of its power of decomposing organic matter of most kinds. Sodium hydroxide melts at 318° C. to a clear liquid. The solid is very hygroscopic. If exposed to the air it deliquesces to a strong solution, which, absorbing carbon dioxide from the air, later dries up to transparent crystals of sodium carbonate decahydrate, which finally effloresce.

Caustic soda is one of the most soluble of substances. Much heat is evolved when it dissolves in water. At 0° C. 100 gms. of water dissolve 42 gms. of caustic soda, and at 110° C., 365 gms. There are several hydrates, the only one stable between 12° C. and 62° C. being $NaOH \cdot H_2O$.

Sodium hydroxide is a strong alkali. Its solutions are completely dissociated and consist of water, sodium ions and hydroxyl ions. They are, therefore, excellent conductors of electricity.

Sodium hydroxide is only slightly soluble in alcohol, in contradistinction to caustic potash, which is highly soluble.

Sodium hydroxide is very stable and is not decomposed by heat. It has the typical properties of an alkali (§ 168). Thus it turns litmus blue, and reacts with even the weakest acids and acidic oxides, forming sodium salts and water.

From solutions of salts of all metals except the alkali metals, it precipitates the hydroxide of the metal concerned. These hydroxides often redissolve in excess of caustic soda (cf. § 484). In addition to these properties, common to all alkalis, we may mention its reactions with many of the elements. The usual reaction of caustic soda with an element is to form the *sodium salt of an oxyacid containing the element* and also *hydroyen*, or if such exists, the *hydride of the element or a salt formed from this hydride and caustic soda*. Thus, consider the reactions listed below and further discussed under the headings of the elements concerned :—

$$2NaOH + Si + H_2O = Na_2SiO_3 + 2H_2$$
$$3NaOH + 4P + 3H_2O = 3NaH_2PO_2 + PH_3$$
$$6NaOH + 12S = Na_2S_2O_3 + 2Na_2S_5 + 3H_2O$$ [1]

[1] The reaction is more complex than is here represented.

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$$2NaOH + Cl_2 = NaOCl + NaCl + H_2O$$ [2]
$$6NaOH + 3Cl_2 = NaClO_3 + 5NaCl + 3H_2O$$
$$2NaOH + 2Al + 2H_2O = 2NaAlO_2 + 3H_2$$
$$2NaOH + Zn = Na_2ZnO_2 + H_2.$$

Most metals are attacked by fusion with caustic soda in presence of air. Nickel is least affected. Sodium hydroxide in solution has an appreciable action upon glass and porcelain. Fused caustic soda attacks these substances vigorously, and alkali fusions are therefore conducted in silver or nickel vessels.

**232. General Properties of Sodium Salts.**—Sodium salts are colourless unless combined with some coloured acid. They are not, in general, poisonous and are, for the most part, very soluble in water. Sodium pyro-antimonate and sodium magnesium uranyl acetate (§ 267) are among the few insoluble salts of sodium. Sodium salts show a tendency to crystallise with much water of crystallisation. Sodium compounds colour the Bunsen flame a brilliant and pure yellow.

## SODIUM SALTS

*Sodium Hydride NaH* is made by heating the melted metal in a current of hydrogen. It is a solid which dissolves in water, giving caustic soda and hydrogen (§ 190).

*Sodium Borates.*—These are discussed under the heading of Boron (§ 469). They include the salt sodium tetraborate or *borax*, which is of great commercial importance.

**233. Sodium Carbonate, $Na_2CO_3$.**—Sodium carbonate has been known since remote times (§ 222) and has through all history possessed practical uses which have caused it to be a valuable article of commerce. Sodium carbonate is made commercially in very great quantities by four methods:

(1) From naturally occurring soda.
(2) By the Leblanc process, which is gradually becoming obsolete.
(3) By the ammonia-soda or Solvay process.
(4) From electrolytic caustic soda.

**234. Native Soda.**—An important source of soda supply is native sodium carbonate found in solution and as dry deposits around and in certain lakes in various parts of the world, notably at Magadi, in British East Africa, and also in Lower Egypt, and in California.

Some 200 million tons of native soda are contained in the Magadi deposits. This is calcined, and the anhydrous sodium carbonate is exported. Native soda suffers from the high cost of freight, but

[2] Bromine and iodine react similarly.

in the opinion of some experts it is possible that it may largely displace artificially-produced soda.

**235. The Leblanc Process.**—The Leblanc or black-ash process is no longer in use in this country, having been ousted by the development of the ammonia-soda and electrolytic processes, and also by the manufacture of hydrochloric acid from electrolytic chlorine (§§ 230, 1053), of which the supply often exceeds the demand.

The process took place in two stages (§ 1052). First of all, sodium chloride common salt, was treated with sulphuric acid, forming at first sodium hydrogen sulphate and hydrogen chloride. The sodium hydrogen sulphate reacted at a red heat with more sodium chloride, forming normal sodium sulphate and a further quantity of hydrochloric acid,

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

The hydrogen chloride was dissolved in water and sold as hydrochloric acid.

The sodium sulphate was then ground and mixed with its own weight of chalk and half its weight of coal and coke, and fused in a rotating furnace. The sulphate was reduced to sulphide, which then reacted with the calcium carbonate, forming sodium carbonate and calcium sulphide

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The mixture of sodium carbonate and calcium sulphide was extracted with water and the sodium carbonate was crystallised out. The insoluble calcium

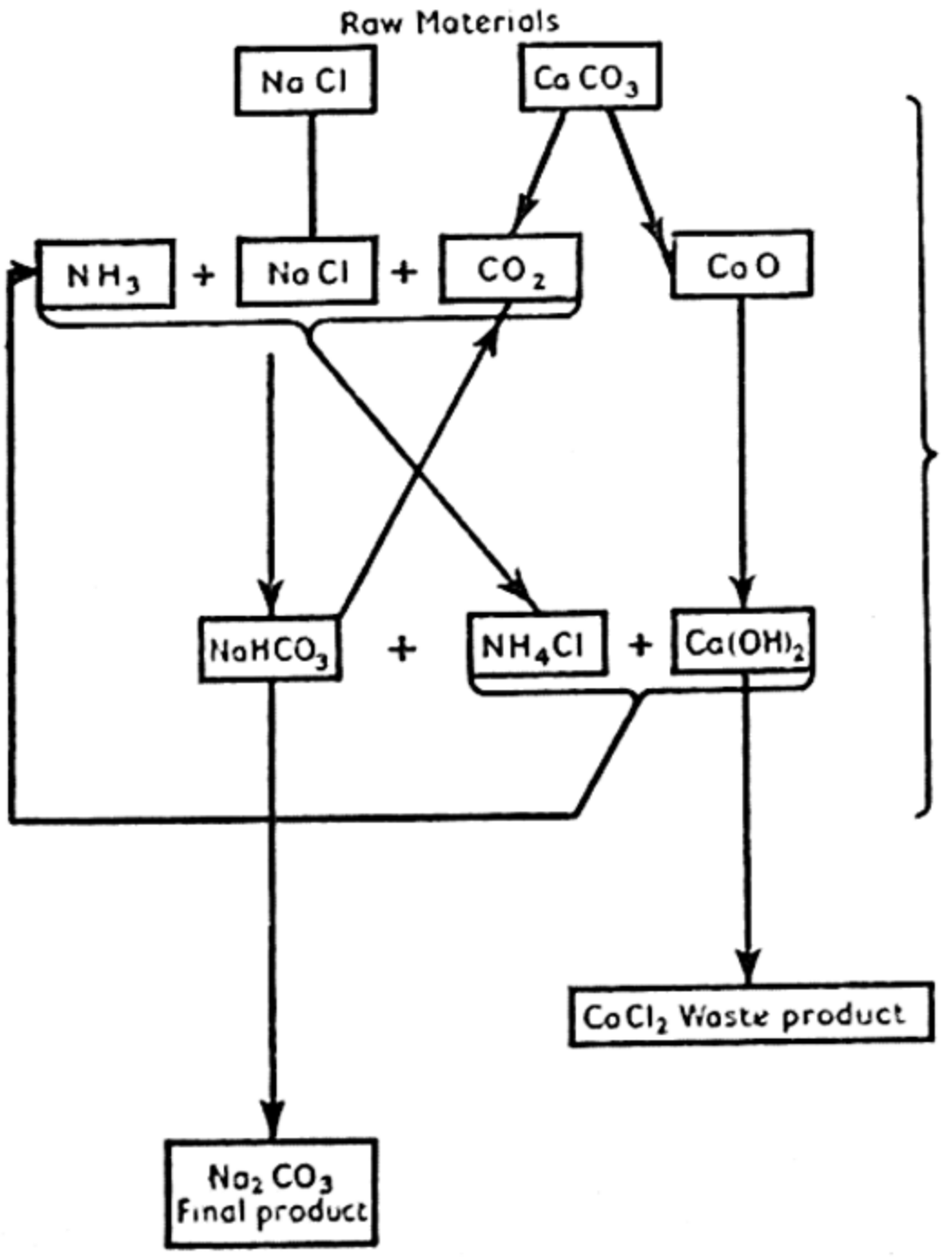


FIG. 75.—Solvay Process. Raw materials, intermediates, and final products.

sulphide, known as alkali waste, was often treated for recovery of sulphur (§ 883).

**236. The Ammonia-Soda Process.**—The Solvay or ammonia-soda process depends upon the comparatively small solubility of sodium bicarbonate. The process involves three stages :—

(1) Brine is saturated first with ammonia gas and then with carbon dioxide. The latter two gases form ammonium and bicarbonate ions,

$$NH_3 + H_2O + CO_2 = NH_4^+ + HCO_3^-.$$

The bicarbonate ion and sodium ion exceed the solubility product of the sparingly soluble sodium bicarbonate, which is precipitated, and ammonium and chloride ions remain in solution,

$$NH_4^+ + HCO_3^- + Na^+ + Cl^- = [Na]^+ [HCO_3]^- + NH_4^+ + Cl^-$$

(2) The solid sodium bicarbonate is calcined, forming sodium carbonate, carbon dioxide and steam.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

If crystallised soda is required the product is recrystallised from water.

(3) The ammonium chloride solution is reconverted into ammonia by heating it with lime,

$$2Cl^- + 2NH_4^+ + Ca^{++} + 2OH^- = 2NH_3 + 2H_2O + Ca^{++} + 2Cl^-.$$

The ammonia being used over and over again, the only materials actually used up are chalk and salt, while the waste product is calcium chloride. The latter product is of little value, and the fact that in this process the chlorine of the sodium chloride is lost renders it open to severe competition from the electrolytic process.

The actual process is carried on in six chief stages.

(1) *Raw Materials.*—Brine is usually obtained by direct pumping from the

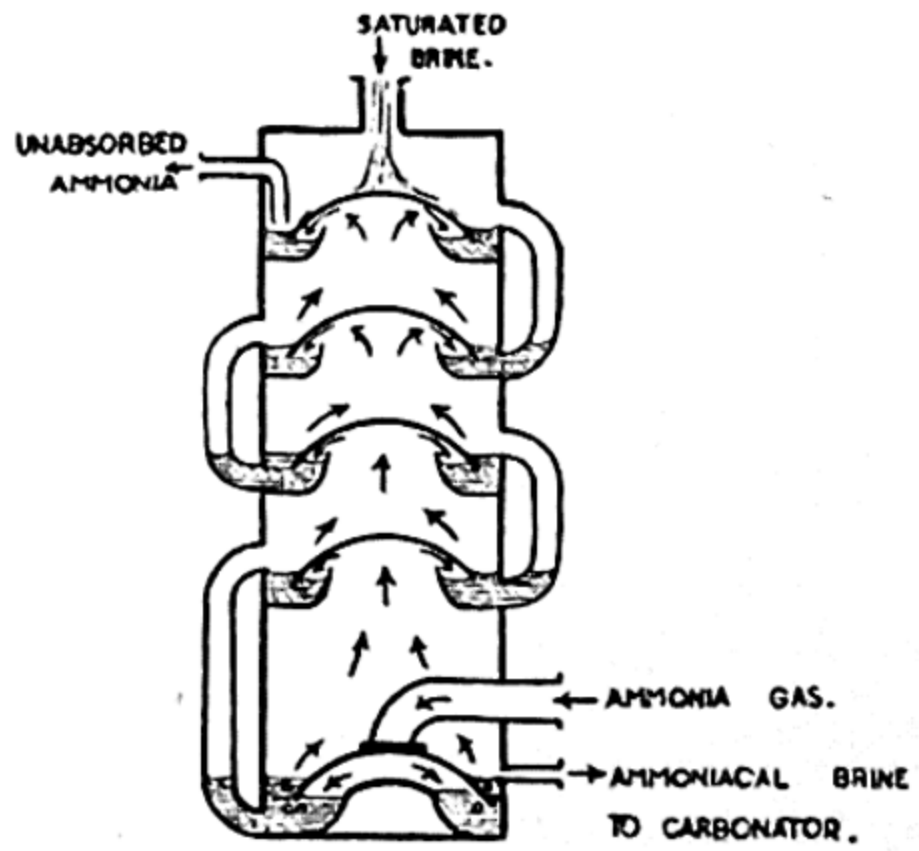


FIG. 76.—Ammonia absorber.

mine. A concentrated solution, containing about 30 gms. of salt per 100 c.c., is required.

Carbon dioxide is obtained by heating limestone in kilns. In this way carbon dioxide is obtained for stage 3 and lime for stage 6.

$$CaCO_3 = CO_2 + CaO.$$

(2) *Production of Ammoniacal Brine.*—Ammonia gas obtained in stage 6 of the process is made to pass up a tower, shown in Fig. 76, down which the

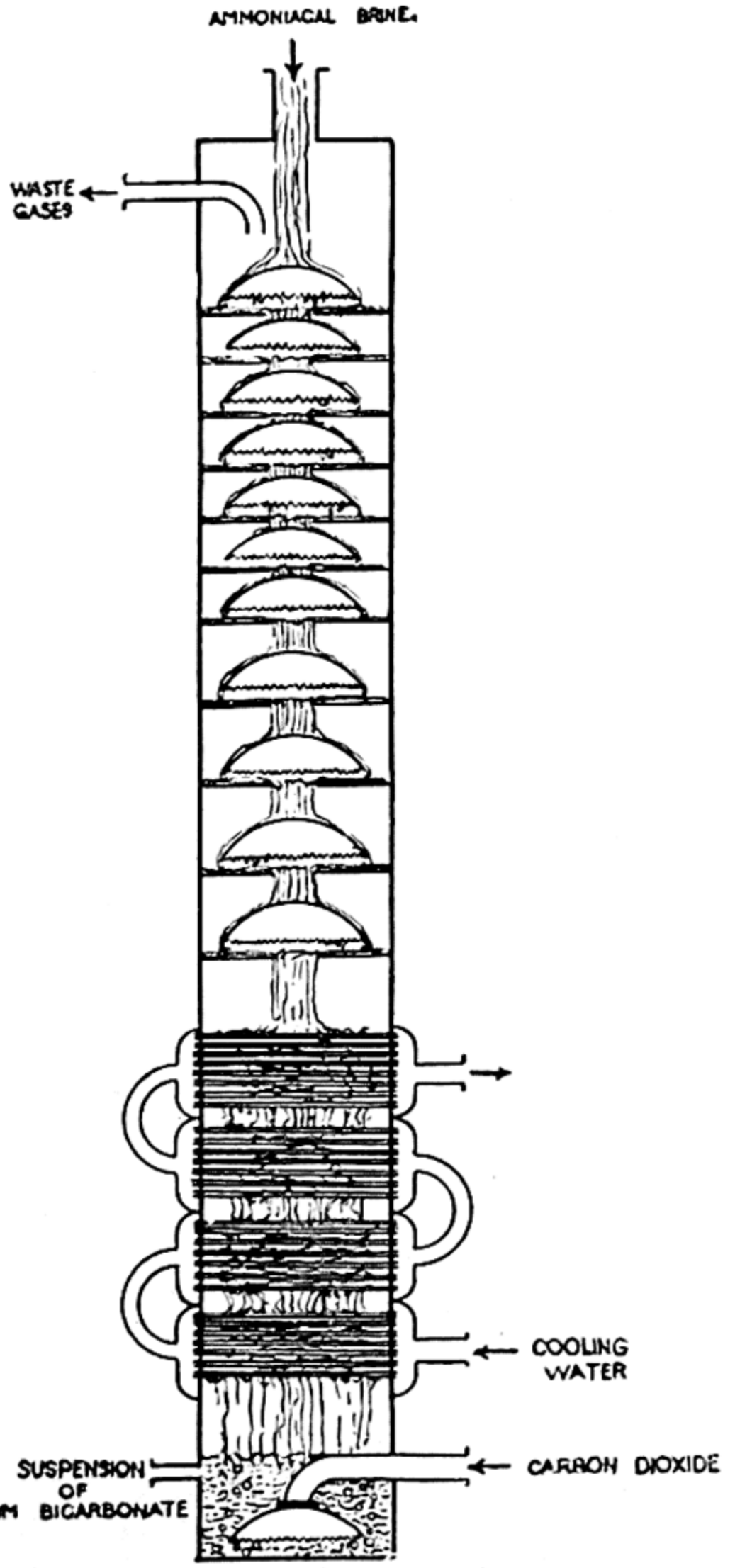


FIG. 77.—Solvay tower.

brine is flowing. The arrangement of cast-iron "mushrooms" and overflow pipes, as shown, ensures that the ammonia gas comes into good contact with the brine. The brine is cooled by means of cold water pipes, for the combination of ammonia with water produces much heat and hot water dissolves less gas than cold.

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(3) The brine, containing *c.* 28 per cent. of sodium chloride and about 7·5 per cent. of ammonia, is allowed to deposit any precipitated calcium carbonate (cf. § 200 (*a*), on hardness of water), and is then run down a *Solvay tower* (Fig. 77), where it passes over a series of serrated mushroom-shaped plates.

Carbon dioxide prepared in stage 1 is pumped up the tower and reactions.

$$NH_3 + CO_2 + H_2O = NH_4^+ + HCO_3^-$$

$$NH_4^+ + HCO_3^- + Na^+ + Cl^- = NaHCO_3 + NH_4^+ + Cl^-$$

take place. The liquor runs out at the bottom of the tower, carrying with it the fine crystals of sodium bicarbonate.

(4) The liquid consists of a suspension of solid sodium bicarbonate in a solution containing various salts, but notably ammonium chloride. It is filtered by vacuum and the bicarbonate washed free from other salts as far as is economically possible.

(5) The sodium bicarbonate is calcined in two stages. First, the adherent ammonia and most of the combined carbon dioxide is driven off by gentle heating in a closed pan furnished with a gas exit. The gases are used again in stages 2 and 3.

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The last traces of carbon dioxide are removed by mechanically raking the partly roasted carbonate through a deep and long iron trough heated by fire beneath.

(6) The residual liquor containing the ammonium chloride (stage 4) is mixed with milk of lime obtained by slaking the lime obtained in (1). Ammonium hydroxide is formed and remains in solution.

$$Ca^{++} + 2OH^- + 2NH_4^+ + 2Cl^- = Ca^{++} + 2Cl^- + 2NH_3 + 2H_2O.$$

The liquor is run down a tower somewhat resembling the carbonator tower (Fig. 76) up which steam is blown. The current of steam may be so arranged that almost all the steam condenses, raising the liquor to 100° C., and so volatilising the ammonia. This, with some steam, passes out of the top of the tower and so passes to the ammonia absorber (stage 2).

**237. Electrolytic Process.**—The electrolysis of sodium chloride solution (§ 230) yields caustic soda and chlorine.

The former is now frequently converted into sodium carbonate by the action of carbon dioxide,

$$2Na^+ + 2OH^- + CO_2 = 2Na^+ + CO_3^{--} + H_2O.$$

The chlorine is either used for bleaching powder or may be converted into hydrochloric acid by combining it with the hydrogen obtained at the cathode of the electrolytic cell (*v.* § 1052). Where electrical energy is cheap, as in America, the process is an ideal one; for there are no waste products.

Sodium chloride solution is electrolysed in a cell of the diaphragm type such as that shown in Fig. 73. The caustic soda formed is converted into sodium carbonate by passing crude carbon dioxide (furnace gases, gas engine

exhaust, etc.) through the liquid. A 30 per cent. solution of sodium carbonate containing a little salt is obtained and is purified by crystallisation.

**238. Purification of Sodium Carbonate.**—Impure sodium carbonate may be purified by dissolving it and adding a little lime. This reacts with the sodium carbonate, forming caustic soda, which then removes any bicarbonate present.

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH$$
$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O.$$

The solution is recrystallised several times to remove sulphates, chlorides, etc.

Pure anhydrous sodium carbonate is best made by washing sodium bicarbonate to remove soluble impurities, drying it and heating to 200–300° C. until no further change of weight occurs.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

**239. Properties of Sodium Carbonate.**—Sodium carbonate exists as anhydrous salt and also as a monohydrate and decahydrate. Two heptahydrates also exist, one of which is unstable and the other stable only between 30° C. and 37·5° C.

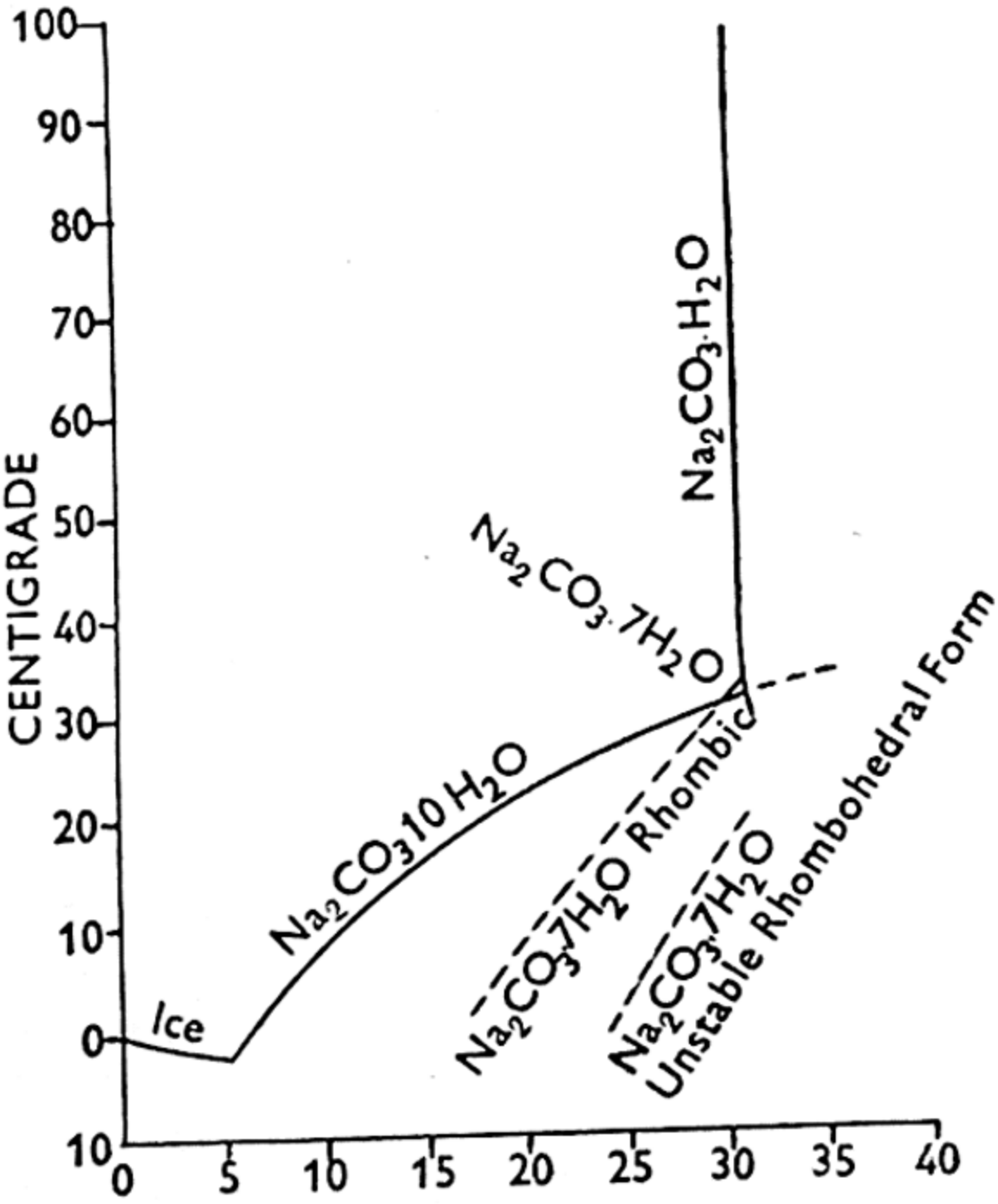



FIG. 78.

Anhydrous sodium carbonate is a white solid, which melts at a red heat (850° C.). It combines with water, becoming hot and forming the monohydrate.

When crystallised from water in the ordinary way (below 32·0° C.) the decahydrate $Na_2CO_3 . 10H_2O$ (soda crystals, washing soda) is

formed in large transparent crystals. This salt is efflorescent, gradually forming the monohydrate when exposed to air; long exposure to air produces some bicarbonate. When heated it melts at 35° C., and on further heating deposits the monohydrate.

*Sodium carbonate heptahydrate* $Na_2CO_3 . 7H_2O$.

The following method may be used to make the heptahydrate. Forty parts of the decahydrate are boiled in a flask with 8 to 10 parts of water till all is dissolved and no monohydrate deposited. The flask is closed with a cork fitted with two glass tubes. Alcohol is poured in above the salt. As the alcohol diffuses into the liquid, rectangular plates of the salt crystallise out. The salt is stable between 30° C. and 37·5° C. only.

The relationship of the hydrates and their solubilities are illustrated by the diagram. (Fig. 78).

Sodium carbonate, together with the carbonates of potassium, rubidium, and cæsium, is exceptional in that it is soluble in water and is not decomposed by heat, but, in other respects, has the usual properties of carbonates (§ 567).

The solution is strongly alkaline on account of the *hydrolysis* of the salt (§ 121).

Sodium carbonate solution consists of sodium and carbonate ions,

$$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{--}.$$

The latter combines with some of the hydrion furnished by the water, forming the weak acid, carbonic acid,

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$CO_3^{--} + 2H^+ \rightleftharpoons H_2CO_3.$$

But the quantities of hydrion and hydroxyl ion in water are given by

$$[H^+]\,[OH^-] = 10^{-14},$$

and so the removal of hydrion results in the liberation of hydroxyl ion $OH^-$ and the solution reacts alkaline.

Sodium carbonate is used to soften water on a domestic scale. The alkaline properties of its solution give it an emulsifying action on grease and make it a valuable cleaning material. Other uses are found for the salt in glass-making, the manufacture of borax and "water-glass." It enters into the composition of many soap-powders.

**240. Sodium Bicarbonate $NaHCO_3$** is formed in the Solvay process, and may also be made by passing a stream of carbon dioxide through concentrated solution of normal sodium carbonate. The bicarbonate, which is much less soluble than the normal salt, is precipitated,

$$CO_2 + H_2O = H_2CO_3$$
$$CO_3^{--} + H_2CO_3 = 2HCO_3^-$$
$$Na^+ + HCO_3^- = NaHCO_3$$

Sodium bicarbonate forms white crystals of a pleasant alkaline

taste. One hundred grams of water dissolve only 8·2 gms. of the salt at 10° C. At 100° C. the salt decomposes, forming carbon dioxide and the normal carbonate.

Sodium bicarbonate solution is slightly alkaline, owing to hydrolysis. The reasons for this behaviour are the same as those given under sodium carbonate (§§ 121, 239). It is interesting that we have in sodium bicarbonate an acid salt with an alkaline reaction.

**241. Sodium Cyanide.**—Sodium cyanide is prepared on the large scale from coal-gas and also from sodium, ammonia and carbon.

Most of the world's cyanide is prepared by the action of sodamide (p. 274) on red-hot charcoal.

Melted sodium is treated with ammonia at low temperatures (300–400° C.) and the sodamide obtained is run on to red-hot charcoal, forming the cyanide. The reactions are :—

(1) Formation of sodamide,

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

(2) Reaction of this with carbon to form sodium cyanamide,

$$2NaNH_2 + C = Na_2N \,.\, CN + 2H_2.$$

(3) Reaction of the sodium cyanamide with carbon, forming sodium cyanide,

$$Na_2N \,.\, CN + C = 2NaCN.$$

A certain amount of crude cyanide suitable for gold recovery (§ 324) is made by fusing crude calcium cyanamide (nitrolim) with common salt or sodium carbonate,

$$CaCN_2 + C + 2NaCl = 2NaCN + CaCl_2.$$

Coal gas in its crude condition (§§ 546, 550) contains hydrocyanic acid, HCN. One of the best processes for converting this into sodium cyanide is the following: The hydrocyanic acid and the ammonia in the gas are absorbed by solutions of copper salts, forming ammonium cuprocyanide, $NH_4]_2[Cu(CN)_3]$.

This is treated with dilute sulphuric acid, and hydrocyanic acid is liberated and is absorbed in caustic soda, forming sodium cyanide,

$$(NH_4)_2Cu(CN)_3 + H_2SO_4 = (NH_4)_2SO_4 + 2HCN + CuCN$$
$$NaOH + HCN = NaCN + H_2O.$$

Insoluble cuprous cyanide CuCN is precipitated and is returned to the absorber, where it again forms fresh cuprocyanide,

$$2NH_3 + 2HCN + CuCN = (NH_4)_2Cu(CN)_3.$$

$H_2S$ does not interfere, for cuprous sulphide itself reacts to form the cuprocyanide. About 2 lbs. of sodium cyanide per ton of coal can be obtained. Another process for recovery of cyanides from coal gas is described in § 550.

The properties of sodium cyanide are discussed in § 575.

Like all sodium salts of weak acids, it is strongly hydrolysed. Its

solution is, therefore, strongly alkaline and smells of hydrocyanic acid. Like all cyanides, it is very poisonous.

**242. Salts of Sodium and Nitrogen.**—*Sodium nitrite* $NaNO_2$ is prepared commercially by reducing sodium nitrate with carbon and lime. Many other oxidisable substances, such as lead or iron, may replace the carbon and lime, and it is produced, though less readily, by heating sodium nitrate alone,

$$2NaNO_3 = 2NaNO_2 + O_2$$

$$2NaNO_3 + C + Ca(OH)_2 = 2NaNO_2 + CaCO_3 + H_2O.$$

The addition of lime removes the carbon dioxide as soon as formed.

Sodium nitrite forms white crystals when pure but is usually slightly yellow. It is very soluble in water, 100 gms. of which dissolve 83·3 of the salt at 15° C. Its reactions are discussed in § 732. It finds considerable use in the manufacture of dyestuffs.

*Sodium Nitrate* $NaNO_3$.—This salt occurs naturally in vast quantities in Chili, associated with some 30 to 60 per cent. of clay, etc., from which it is freed by recrystallisation. The origin of the deposits is obscure, but possibly they are derived from the decay of masses of seaweed.

It forms white, somewhat hygroscopic, crystals, very soluble in water. At 20° C. 100 gms. of water dissolve 88 of the salt, and at 100° C., 175·5 gms. Its properties resemble, in general, those of the other nitrates of the alkali metals, and are discussed in § 750.

Enormous quantities are used in agriculture as a fertiliser, and also in the chemical industry, for the manufacture of potassium nitrite, sodium nitrite and nitric acid.

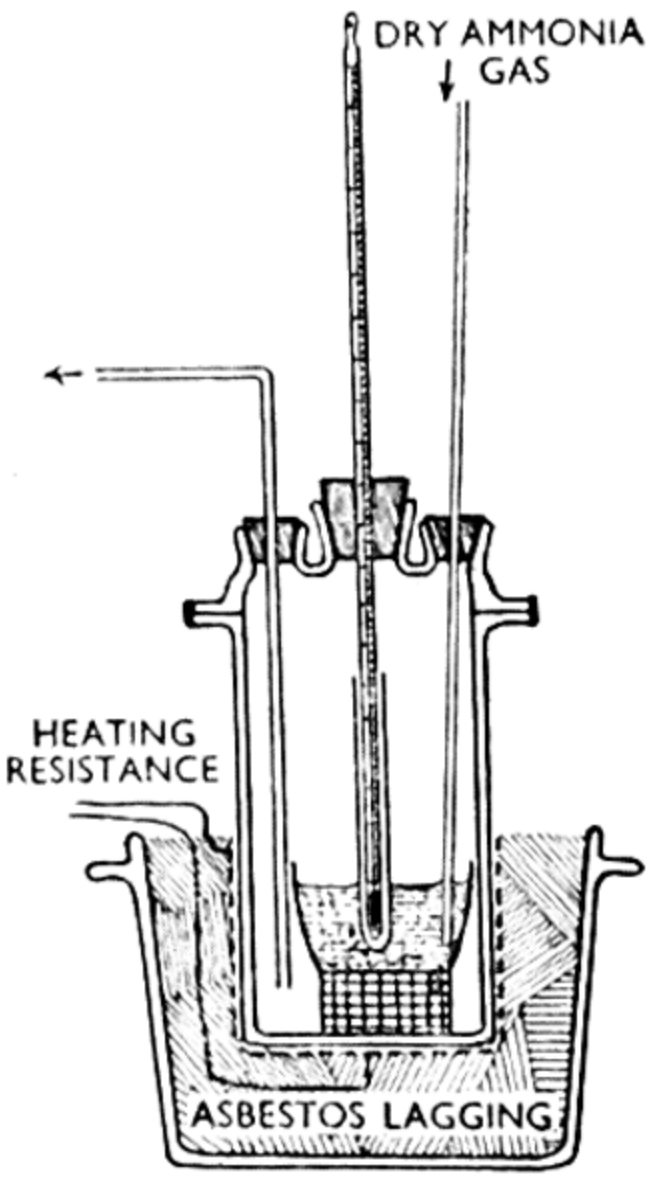



FIG. 79.—Preparation of sodamide. (Wöhler and Stang-Lund, 1918.)

*Sodium amide or sodamide* $NaNH_2$ is produced by passing a stream of dry ammonia gas over metallic sodium at 300°–400°, contained in an iron vessel. Sodium is heated in an iron vessel surrounded by a porcelain outer vessel, through which a current of dry ammonia gas is passed. The reaction

$$2Na + 2NH_3 = 2NaNH_2 + H_2$$

takes place, and in the course of some hours pure sodamide only remains.

Sodamide is a waxy solid, white when pure. When heated it melts at 210° C.

It is decomposed by water, yielding caustic soda and ammonia, great heat being evolved.

$$NaNH_2 + H_2O = NaOH + NH_3.$$

Heated in a current of carbon dioxide it yields sodium carbonate and cyanamide,

$$2NaNH_2 + 2CO_2 = Na_2CO_3 + H_2O + CN \cdot NH_2.$$

Heated in a current of nitrous oxide it yields sodium azide,

$$NaNH_2 + N_2O = NaN_3 + H_2O.$$

**243. Phosphates of Sodium.**—Several sodium phosphates exist (*v.* §§ 200(d), 782).

*Normal sodium orthophosphate* $Na_3PO_4$ is usually made by the action of the theoretical quantity of caustic soda upon disodium hydrogen phosphate,

$$Na_2HPO_4 + NaOH \rightleftharpoons Na_3PO_4 + H_2O,$$

*or*

$$HPO_4^{--} + OH^- = PO_4^{---} + H_2O.$$

Solutions of normal sodium phosphate are strongly alkaline as a result of the hydrolysis indicated by the reversible character of the above reaction (*v.* § 121).

*Disodium hydrogen phosphate* is usually met with as the dodecahydrate $Na_2HPO_4 \cdot 12H_2O$. It is made by the neutralisation of phosphoric acid, employing phenolphthalein as an indicator. It forms white crystals soluble in water. One hundred grams of water dissolve 3·5 gms. at 10° C.: and 102 gms. at 100° C. Several hydrates exist. When heated, disodium hydrogen phosphate yields *sodium pyrophosphate*,

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

Its solutions are very slightly acid, being acid to phenolphthalein but alkaline to methyl orange (pH value, *c.* 4·5).

*Sodium dihydrogen orthophosphate* $NaH_2PO_4$ forms a monohydrate and dihydrate. It is made by the action of phosphoric acid on disodium hydrogen phosphate.

$$H_3PO_4 + Na_2HPO_4 = 2NaH_2PO_4,$$

*or*

$$HPO_4^{--} + H_3PO_4 = 2H_2PO_4^-.$$

It forms white, very soluble crystals, which yield an acid solution. When heated carefully *sodium hydrogen pyrophosphate* $Na_2H_2P_2O_7$ is obtained.

**244. Sulphides of Sodium.**—It is certain that several of these exist, the compounds NaSH, $Na_2S$, $Na_2S_2$, $Na_2S_3$, $Na_2S_5$ having been prepared.

*Sodium Hydrosulphide* NaSH.—Sodium hydrogen sulphide exists in a solution of sodium hydroxide saturated with hydrogen sulphide.

$$2NaOH + H_2S = Na_2S + 2H_2O$$
$$Na_2S + H_2S = 2NaSH.$$

The solid can be prepared by the action of hydrogen sulphide on sodium ethoxide,

$$H_2S + NaOC_2H_5 = NaSH + HOC_2H_5,$$

the solid salt being precipitated by addition of ether. It is a white deliquescent solid and has the usual properties of a sulphide.

When heated it forms sodium monosulphide.

*Sodium monosulphide* $Na_2S$ is formed by the action of hydrogen sulphide on caustic soda.

$$2NaOH + H_2S = Na_2S + 2H_2O.$$

The solid salt is best made by heating sodium hydrogen sulphide,

$$2NaSH = Na_2S + H_2S.$$

On the industrial scale it is made by heating sodium sulphate with coal,

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$

It is a faintly buff-coloured solid, which forms numerous hydrates with water. Its solutions are strongly alkaline owing to hydrolysis and have the odour of hydrogen sulphide (*v.* § 121). It has the usual properties of a sulphide (§ 905).

*Sodium Polysulphides* ($Na_2S_n$ when $n$ is 2–5). There is a good deal of doubt as to what sodium polysulphides actually exist. As many as nine different compounds have been described, but probably some of these are only mixtures of sodium pentasulphide and sodium monosulphide.

These salts are formed by melting sodium with sulphur,

$$2Na + 3S = Na_2S_3,$$

or by boiling sulphur with caustic soda,

$$6NaOH + 12S = Na_2S_2O_3 + 2Na_2S_5 + 3H_2O,$$

or by heating sodium monosulphide with sulphur,

$$Na_2S + 4S = Na_2S_5.$$

The polysulphides are yellow in colour. In air they oxidise to thiosulphates and deposit sulphur,

$$2Na_2S_5 + 3O_2 = 2Na_2S_2O_3 + 6S.$$

Treated with acids they form hydrogen persulphide or hydrogen sulphide and sulphur (*v.* § 907).

*Uses.*—Sodium monosulphide is considerably used in the dye industry for preparing the very fast "sulphide" dyes. It is also employed for stripping the hair from hides.

**245. Sulphites of Sodium.**—*Sodium sulphite* $Na_2SO_3$. The form of this salt commonly met with is the heptahydrate $Na_2SO_3 . 7H_2O$. It is made by the action of sulphur dioxide on caustic soda solution, the action being stopped when the solution becomes neutral,

$$2NaOH + SO_2 = Na_2SO_3 + H_2O.$$

It forms colourless monoclinic crystals soluble in water (100 gms. water dissolve 20·0 gms. anhydrous salt at 10·5° C.).

In its chemical behaviour it resembles the other sulphites (§ 917).

*Sodium Hydrogen sulphite* $NaHSO_3$ is formed when sodium carbonate solution is saturated with sulphur dioxide,

$$Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2.$$

*Sodium pyrosulphite or meta-bisulphite* $Na_2S_2O_5$ is formed also under the above conditions and separates out when the solution is kept cold.

$$Na_2CO_3 + 2SO_2 = Na_2S_2O_5 + CO_2.$$

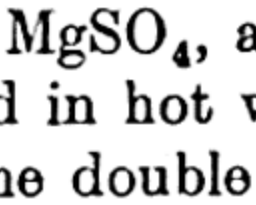
It behaves like an acid sulphite, and is used in photography.

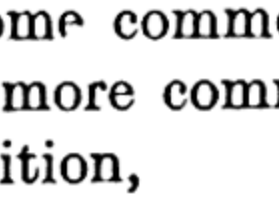
*Sodium potassium sulphite* $NaKSO_3$ can be prepared by the action of (*a*) sodium hydrogen sulphite on potassium carbonate, and (*b*) potassium hydrogen sulphite on sodium carbonate,

(*a*) $2NaHSO_3 + K_2CO_3 = 2NaKSO_3 + H_2O + CO_2.$

(*b*) $2KHSO_3 + Na_2CO_3 = 2KNaSO_3 + H_2O + CO_2.$

Röhrig and Schwicker claimed to have isolated two different compounds by methods (*a*) and (*b*). These they supposed to have the formulæ,




This work has, however, been disproved (§ 916).

**246. Sulphates of Sodium.**—*Sodium sulphate* $Na_2SO_4$. Normal sodium sulphate exists as the anhydrous salt $Na_2SO_4$, the unstable heptahydrate $Na_2SO_4 . 7H_2O$, and the decahydrate $Na_2SO_4 . 10H_2O$. The latter substance is known as Glauber's salt, having been discovered by the 'iatro-chemist' Glauber in the seventeenth century, and used by him medicinally as a purgative.

Anhydrous sodium sulphate is made by the method described in § 1052. It is also prepared from the salts present in the Stassfurt deposits.

The insoluble residues from the manufacture of potassium chloride from carnallite (§265) contain much magnesium sulphate in the form of kieserite $MgSO_4$, and also some common salt. These residues are dissolved in hot water and more common salt added. In consequence of the double decomposition,

$$10H_2O + Mg^{++} + SO_4^{--} + 2Na^+ + 2Cl^-$$
$$= [Na]_2^+ [SO_4]^{--} . 10H_2O + Mg^{++} + 2Cl^-$$

hydrated sodium sulphate $Na_2SO_4 . 10H_2O$ crystallises out, being less soluble in cold water than any of the other salts which can be formed from these four ions.

Anhydrous sodium sulphate is a white solid unaffected even by strong heating. Below 32·4° C. it combines with water, forming the decahydrate, and above that temperature the decahydrate decomposes and forms the anhydrous salt. The solubilities and transition points are shown in the solubility curve (Fig. 31).

The decahydrate forms long colourless crystals. It readily forms supersaturated solutions. The heptahydrate, which is always unstable in presence of the decahydrate, but is stable by itself, is formed by cooling such a supersaturated solution to 5° C.

Sodium sulphate has the usual properties of sulphates (§ 938). It is reduced to the sulphide when it is heated with charcoal.

Hydrated sodium sulphate is used in medicine and in freezing

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mixtures. It is also used in the manufacture of glass (*q.v.*). It is also employed in large quantities for making the brown paper pulp used for the very strong kraft-papers. The wood is boiled with sodium sulphate, which is partly reduced to sulphides, etc.

*Sodium hydrogen sulphate, sodium bisulphate*, $NaHSO_4$ is made by the action of sulphuric acid on common salt at ordinary temperatures, or by mixing the correct proportions of dilute sulphuric acid and caustic soda solution and crystallising the solution,

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$NaOH + H_2SO_4 = NaHSO_4 + H_2O.$$

Sodium hydrogen sulphate is a white solid, which is found either as small crystals of the monohydrate $NaHSO_4 . H_2O$, or in the anhydrous state.

When heated it melts at about 300° C., and near a red heat it decomposes, forming sodium sulphate and sulphuric acid,

$$2NaHSO_4 = Na_2SO_4 + H_2SO_4.$$

In solution it behaves like a mixture of sodium sulphate and sulphuric acid, since it ionises, forming sodium ion, hydrion, and the sulphate and acid sulphate ions,

$$NaHSO_4 \rightleftharpoons Na^+ + HSO_4^- \rightleftharpoons Na^+ + H^+ + SO_4^{--}.$$

In industry it is a by-product of nitric acid manufacture (§ 736). It is used in the manufacture of hydrochloric acid (§ 1052).

In the laboratory, sodium hydrogen sulphate can be used in place of sulphuric acid at temperatures above the boiling-point of the latter. Thus certain oxides, such as aluminium oxide, which are hardly attacked by sulphuric acid, may be converted into sulphates by fusion with this salt,

$$Al_2O_3 + 6NaHSO_4 = Al_2(SO_4)_3 + 3Na_2SO_4 + 3H_2O.$$

The fused salt has also been used as a heating bath for determining the melting points of substances melting above *c.* 350° C.

*Sodium persulphate* $Na_2S_2O_8$.—Solutions may be prepared by electrolysis of concentrated sodium sulphate solution (*v.* § 946). The solid salt can be made by the action of sodium carbonate on ammonium persulphate.

*Sodium thiosulphate* $Na_2S_2O_3 . 5H_2O$ is prepared as described in § 924. It forms colourless crystals very soluble in water, 65 gms. dissolving in 100 gms. of water at 15° C.

When heated it first gives off water of crystallisation, and then decomposes above 200° C. to sodium sulphate and pentasulphide.

$$4Na_2S_2O_3 = Na_2S_5 + 3Na_2SO_4.$$

Its use in photography is described in § 318.

SODIUM CHLORIDE.

**247. Occurrence and Manufacture.**—This salt has, of course, been known since the most ancient times. It occurs in all animal fluids to the extent of some 2·5 per cent. Sodium chloride is found native as *rock salt* or *halite*. This material varies from transparent colourless cubic crystals to a reddish or brownish mass containing a certain amount of insoluble impurity, chiefly iron oxide. Deposits of rock salt are found in many parts of the world. In Great Britain, the deposits at Northwich, in Cheshire, are the most important. On the Continent, the deposits at Stassfurt are very extensive, while another important mine is at Wieliczka, in Galicia (Plate XIA).

These salt deposits arise from the drying up of inland seas, lagoons or salt lakes. It has proved difficult, however, to reconcile the great depth of these deposits, 2,000 feet or more in the case of the Stassfurt deposits, with the drying up of a simple salt lake, for even supposing the water to have been as salt as that of the Dead Sea, 2,000 feet of salt imply about two miles depth of water. The most likely explanation is that an inland lagoon existed separated from the open sea by a bar, over which sea water broke in stormy weather. In this way the lagoon would be refilled yearly with sea water in the winter storms, while the evaporation of summer would deposit yearly a layer of salt. We must suppose that a slow geological subsidence lowered the lagoon bottom a few inches yearly, and that

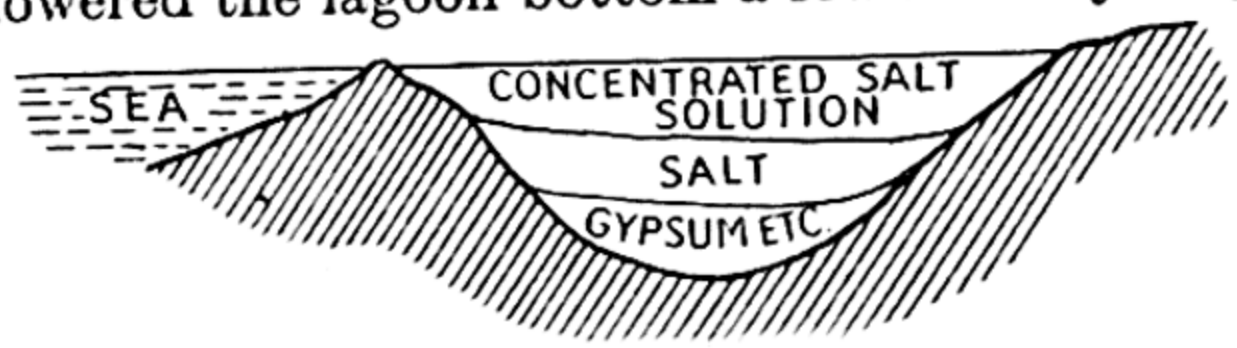


FIG. 80.—Formation of salt beds.

there accumulated in this way first a deposit of the least soluble salts in sea water, such as gypsum, and then a vast deposit of salt. The more soluble and less abundant salts would remain in solution to the last, and we would therefore find, as at Stassfurt, a layer of salt below covered with magnesium and potassium salts above.

The process has probably often also been complicated by intervening upheavals of land.

Salt occurs also in sea water, the average content of which is 2·5 to 3 per cent. Salt lakes such as the Dead Sea and the Great Salt Lake of Utah contain much more salt. The former contains some 22 per cent., and the latter as much as 30 per cent.

**248. Manufacture of Common Salt.**—Salt is either mined or extracted from deposits as *brine*, or obtained from sea water by evaporation.

*Salt from Salt Mines.*—Salt as obtained by mining is usually impure,

containing magnesium and calcium salts, iron oxide, etc. It is used in the impure state for some purposes, but is usually purified by solution in water and crystallisation by the method described below.

At Droitwich, water has access to the salt deposits, and a highly concentrated solution of salt is pumped to the surface. In other mines water is allowed to flow into the deposit and the strong salt solution (*c.* 26 per cent.) is pumped up.

The solution of salt so obtained contains some magnesium and calcium salts, and these are removed by crystallisation.

The solution is run into a series of rectangular iron tanks set over a single flue. The tank nearest the fire is the smallest, and they are made progressively larger as they are farther from the fire. The first pan boils, and very small crystals of salt are deposited. These are fished out with shovels and placed, while hot and wet, in wooden moulds. On cooling, the further crystallisation of the mother liquor with which the salt is wet causes the crystals to bind into the familiar blocks of culinary salt. Good qualities of table salt are mixed with a little bone-ash, which prevents the clogging of the crystals when exposed to damp air.

The next pan, the temperature of which is about 60 to 80 degrees, gives a coarse-grained salt used in industrial work, while the remaining pans, at 40 to 60° C., yield successively larger crystals, which are required for the curing of fish and various other purposes.

The magnesium salts remain in solution, while the calcium salts form a hard scale on the pans.

Multiple-effect evaporators are often used. Since scale would seriously affect their working, the brine is softened by the addition of, first, lime, then sodium carbonate. When freed from calcium salts it is evaporated in a series of vessels so arranged that the steam from the first boils the liquid in the second, which is kept at a pressure lower than atmospheric. The steam from this second pan boils more salt solution in a third vessel, which is kept at a still lower pressure by a vacuum pump. The salt falls down the long shafts (Fig. 81) which are of such a length that the weight of the column of brine therein balances the atmospheric pressure. These multiple-effect evaporators use the minimum of fuel for a given amount of water evaporated.

*Salt from Sea Water.*—The composition of sea water is approximately :

| | |
|---|---|
| Water | 96·50 |
| Sodium chloride | 2·72 |
| Magnesium chloride | 0·38 |
| Magnesium sulphate | 0·17 |
| Calcium sulphate | 0·13 |
| Calcium carbonate | 0·01 |
| Potassium sulphate | 0·08 |
| Magnesium bromide | 0·01 |
| | 100·00 |

The extraction of salt from sea-water is practised only in countries where the sun can be depended on, and where there is little tide, *e.g.*, the Mediterranean regions and the coast of India. A series of lagoons are made, bottomed with puddled clay. Sea water is run into one of these and allowed to evaporate until most of the gypsum and clay, etc., have deposited. It then passes to the second lagoon, where it evaporates until it contains about 25 per cent. of salt. Salt then deposits and is raked into heaps to drain. Occasional showers serve to remove the more soluble impurities, and some of these tend to deliquesce and drain away from the bottom of the heap. The mother liquors are worked for potassium salts and for bromine (*q.v.*). The salt is usually recrystallised.

The total salt production of the world is some 20 million tons a

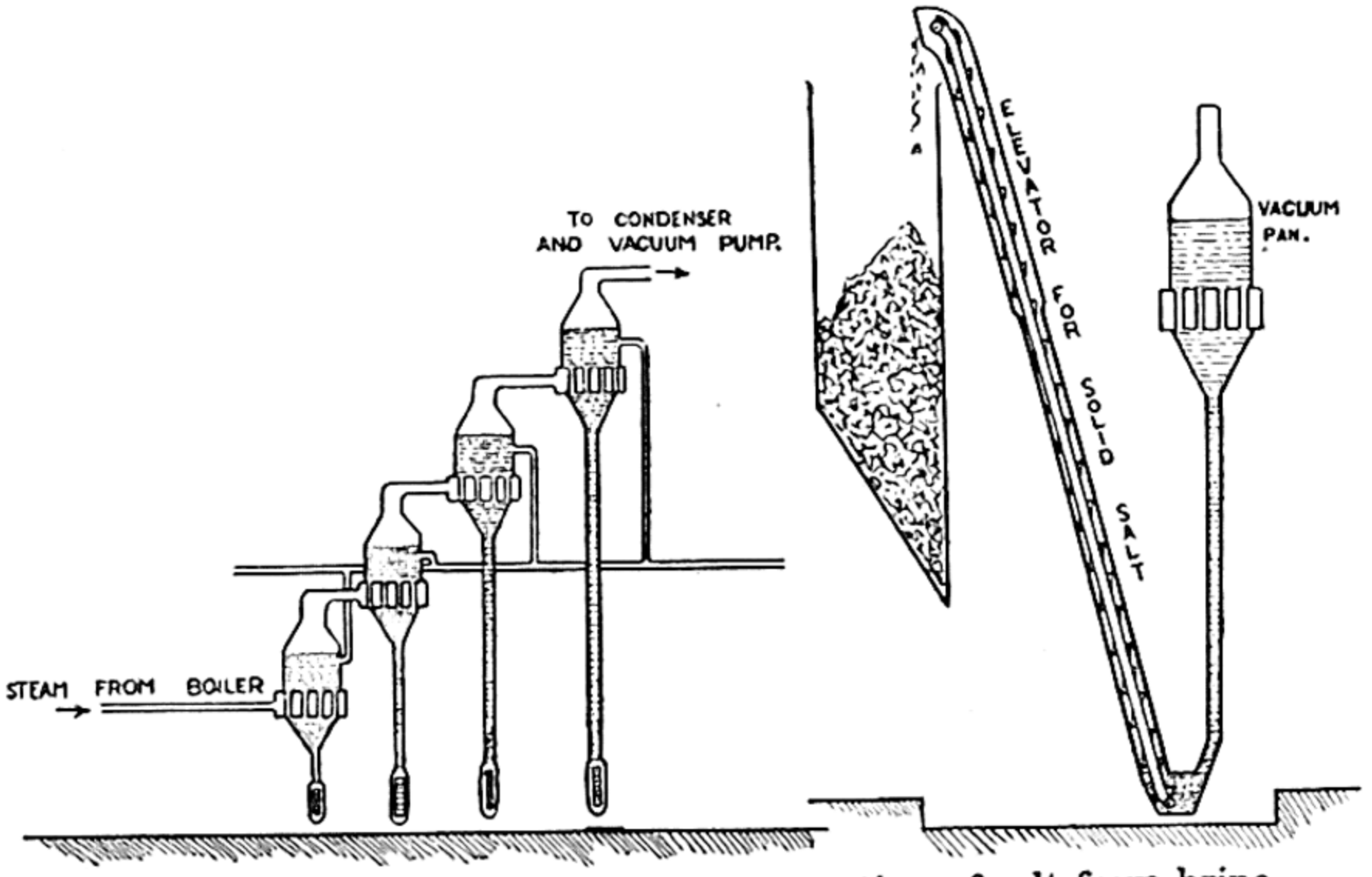


FIG. 81.—Multiple evaporators for preparation of salt from brine.

year or about 22 lbs. per person. About two-thirds of this quantity is used for food.

**249. Purification of Salt.**—For laboratory purposes salt may be purified by saturating a solution of ordinary salt with hydrogen chloride, or by adding concentrated hydrochloric acid to concentrated salt solution. Salt is very much less soluble in concentrated hydrochloric acid (1·6 per cent.) than in water (35·8 per cent.) and it is accordingly precipitated. Other chlorides, which are more soluble and are present in much smaller concentration, are not precipitated in this way. The crystals are filtered off, washed with water, dried and heated. If required very pure, the precipitation may be repeated and the salt finally fused to remove traces of hydrogen chloride.

**250. Properties of Sodium Chloride.**—Sodium chloride crystallises in cubes, which are colourless when pure. Its taste is well enough known and distinguishes it from all other salts. The density of the pure salt is 2·17, and it melts at about 800° C. It is slightly volatile even at this temperature. Common salt is soluble in water, and its solubility varies but little with the temperature, as the appended figures show.

| Temperature °C. | Grams NaCl dissolving in 100 gms. water. |
|---|---|
| 0 | 35·6 |
| 20 | 35·8 |
| 40 | 36·3 |
| 60 | 37·06 |
| 80 | 38·0 |
| 100 | 39·1 |

It is nearly insoluble in alcohol. Aqueous solutions containing less than 23·6% salt deposit ice when cooled; solutions stronger than 23·6% deposit salt, anhydrous or hydrated ($NaCl \cdot 2H_2O$). The solution of 23·6% strength is that which freezes at the lowest temperature – 22° C., and at this temperature—the eutectic—both ice and salt deposit, and this is the lowest temperature which can be reached by an ice-and-salt freezing mixture.

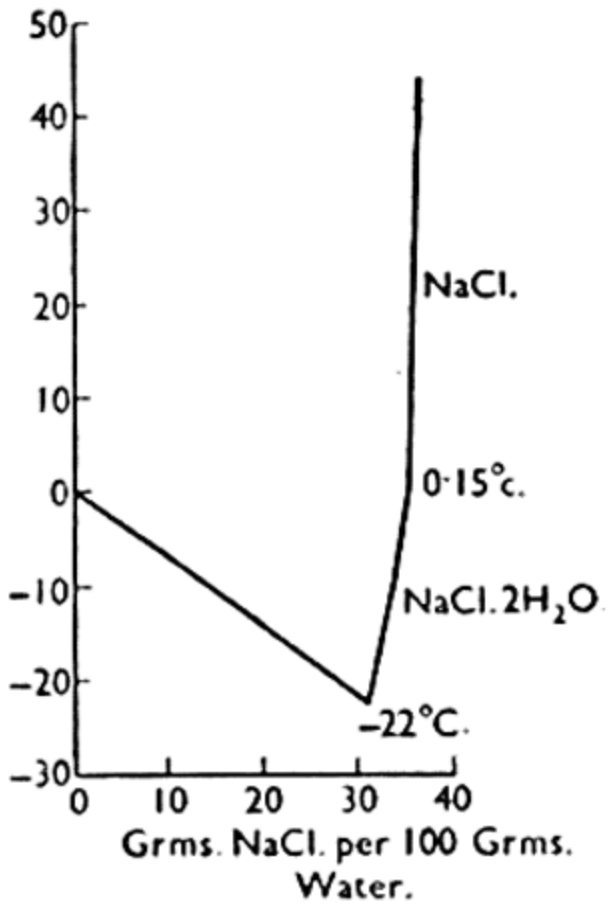


FIG. 82.—Solubility of sodium chloride.

**251. Chemical Properties of Sodium Chloride.**—In general, sodium chloride has the usual properties of sodium salts (§ 232), and of chlorides (§ 1057). With sulphuric acid it yields sodium hydrogen sulphate and hydrogen chloride.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

Its solution precipitates silver chloride from solutions of silver salts, etc.

**252. Uses of Sodium Chloride.**—Sodium chloride finds a vast number of uses. The most important of these are :—

(1) Use as an article of diet and as a preservative for food (hams, butter, fish, meat, etc.).

(2) Use in the manufacture of sodium (§ 223), sodium carbonate (§§ 235–237), hydrochloric acid (§ 1052), sodium hydroxide (§ 230), chlorine (§§ 230, 1041), sodium sulphate (§ 1052).

**253. Other Salts of Sodium and the Halogens.**—*Sodium fluoride* NaF.—Sodium fluoride is a white salt resembling the chloride. It has the usual properties associated with fluorides (§ 1035). It has been used as a mild disinfectant.

*Sodium bromide* and *iodide* are not very much used in chemical practice. They are made by the same methods as the potassium salts (§ 266), and have similar properties. Sodium bromide and iodide form hydrates, $NaBr \cdot 2H_2O$ and $NaI \cdot 2H_2O$.

*Sodium hypochlorite* is discussed in § 1065.

*Sodium chlorate* is made electrolytically by similar methods to potassium chlorate (§ 1071). It has properties similar to those of that salt, but is very much more soluble in water, and is therefore preferred for certain organic oxidations which are carried out in solution. It is widely employed as a weed-killer.

## POTASSIUM K, 39·096

**254. History of Potassium.**—The potassium carbonate obtained by lixiviating wood ash has been known since early times, but was not clearly distinguished from 'natron' or sodium carbonate until the eighteenth century. The metal potassium was isolated by Davy in 1808.

**255. Occurrence of Potassium Compounds.**—The chief source of potash is the Stassfurt salt deposits, which contain vast quantities of *carnallite*, potassium magnesium chloride $KCl \cdot MgCl_2 \cdot 6H_2O$, *kainite* $K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$, and *sylvine* KCl potassium chloride. The extraction of pure potassium salts from these is described in §§ 264, 265. A certain amount of potash was obtained from *orthoclase*, a form of felspar, potassium aluminium silicate, during the Four Years' War of 1914–18, when the German supply of potash was no longer available. The ashes of plants contain a good deal of potassium carbonate. All plants contain potassium salts, which they obtain from the soil. In a state of nature the decay of plant materials returns this to the soil once more. Man however, removes crops from the soil and finally sends the potash down the sewers to the sea. It becomes necessary, therefore, to supply potassium salts to the soil. Kainite is a useful form of potash for this purpose.

It is interesting to note that potassium salts, though quite as

soluble as sodium salts, are not found in appreciable quantity in the sea. It appears that potassium ion is adsorbed by the soil much more readily than sodium ion, and that consequently the former is retained in the soil while the latter is washed out to the sea.

**256. Preparation of Potassium.**—Formerly potassium was made by heating potassium carbonate with carbon,

$$K_2CO_3 + 2C = 2K + 3CO.$$

Explosions often occurred in this process owing to the formation of the explosive potassium carbonyl $K_2(CO)_2$.

The Castner process described under sodium (§ 223) is not satisfactory for potassium, which dissolves in the fused caustic potash. The process employed is the electrolysis of fused potassium chloride.

**257. Properties of Potassium.**—Potassium is a soft white metal. Its density is 0·86. It melts at 62° C. and boils at about 730° C.,[1] producing a green monatomic vapour. Potassium is a good conductor of heat and electricity.

Both potassium and rubidium emit $\beta$-rays. Their radioactivity is, however, exceedingly feeble compared with that of even uranium or thorium. It appears that potassium should be yielding an isotope of calcium as a result of its activity, but the formation of this has not yet been detected.

The chemical properties of potassium are almost identical with those of sodium (§ 224). It is, however, rather more reactive. When dropped on water it decomposes it in the same way as sodium, but more vigorously. Thus the hydrogen evolved by the smallest fragments of potassium in contact with water ignites spontaneously and burns with a lilac coloured flame.

**258. Atomic Weight.**—The atomic weight of potassium has been determined by a similar method to that described under sodium. Richards and Miller found the value 39·114 in 1907, and the value adopted is 39·096 (O = 16). Another method used was the action of heat upon potassium chlorate, a salt obtainable in a state of high purity. 60·846 gms. of potassium chloride are obtained by the action of heat upon 100 gms. of potassium chlorate.

Thus the ratio $\frac{KCl}{KClO_3} = \cdot 60846$. If we call the atomic weight of potassium $x$ and adopt the value for the atomic weight of chlorine given by Richards (35·456) we have

$$\frac{x + 35\cdot456}{x + 35\cdot456 + 3 \times 16\cdot00} = \cdot 60846,$$

which yields the result 39·14.

[1] Widely varying figures have been recorded.

The most probable value is 39·096. Potassium consists of two isotopes of atomic weight, 39·0 and 41·0, the latter only in small proportion.

**259. Oxides of Potassium.**—These are three in number :—

Potassium monoxide $K_2O$,
Potassium dioxide $K_2O_2$,
Potassium peroxide $KO_2$ (formerly written $K_2O_4$).

*Potassium monoxide* $K_2O$ is made by the careful oxidation of potassium in dry oxygen under reduced pressure, the excess of potassium being distilled off *in vacuo*. In its properties it resembles sodium monoxide (p. 260).

*Potassium dioxide* $K_2O_2$ is formed by heating potassium peroxide.

*Potassium peroxide* $KO_2$ is made by burning potassium in air or oxygen,

$$K + O_2 = KO_2.$$

When treated with water it yields hydrogen peroxide, caustic potash and oxygen,

$$2KO_2 + 2H_2O = 2KOH + H_2O_2 + O_2.$$

The formula for this substance should probably be written as,

$$K^+[O - O]^- \quad \text{or} \quad K^+[:\dot{O}.\dot{O}:]^-.$$

**260. Potassium Hydroxide, Caustic Potash, KOH.**—Caustic potash is prepared by methods analogous to those used for the preparation of caustic soda (§ 227).

Potassium hydroxide is a white solid, resembling caustic soda in its corrosive properties. It melts at 360° C. It is very hygroscopic and very soluble in water, 100 gms. of which dissolve 113 gms. of caustic potash at 20° C. and 187 gms. at 100° C. It forms several hydrates.

Its chemical properties are very similar to those of caustic soda (§ 231). It is preferred to the latter for organic work on account of its ready solubility in alcohol.

'Alcoholic potash' is a useful reagent, which acts both as an alkali and as an agent for the removal of halogen hydride. Thus ethyl bromide with aqueous potash yields ethyl alcohol.

$$C_2H_5Br + KOH = C_2H_5OH + KBr,$$

but with alcoholic potash yields ethylene,

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O.$$

Caustic potash is used as a drying agent for gases, and is also useful for absorbing acid gases. Solutions of caustic potash are much used for the latter purpose. Cold caustic potash solution can be made much stronger than cold caustic soda solution, and when it is used

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for absorbing carbon dioxide the extremely soluble potassium carbonate does not crystallise out and block the tubes, etc., as would the less soluble sodium carbonate.

**261. General Properties of Potassium Salts.**—Potassium salts are colourless unless combined with some coloured acid. They have a peculiar "cooling" taste, and in large quantities are poisonous, having a depressant action on the heart. The salts are, in general, stable and fusible without decomposition. All the common potassium salts are freely soluble in water. Potassium salts crystallise, as a rule, with little or no water of crystallisation. The platinichloride $K_2PtCl_6$, and the perchlorate $KClO_4$, the acid tartrate $KHC_4H_4O_6$, and the picrate $KO \cdot C_6H_2(NO_2)_3$, are nearly insoluble in water, and the first three are still less soluble in alcohol (*v.* p. 287).

Potassium compounds colour the Bunsen flame lilac. The colour is due to a line in the red and another in the blue region of the spectrum.

In chemical properties the salts of potassium so nearly resemble those of sodium that it will only be necessary to describe the particulars in which they differ from the corresponding sodium compounds.

**262. Potassium Carbonate, 'Pearlash,' $K_2CO_3$.**—This salt has been known since the earliest times, a solution of the salt made from wood-ash and water being used as a cleaning agent, and also for soap-making. Dioscorides (*c.* A.D. 50), described the preparation of the substance by heating crude wine lees (argol), acid potassium tartrate.

Potassium carbonate is made from potassium chloride or from wood-ash. The ammonia-soda process cannot be adapted for the manufacture of potassium carbonate, for the bicarbonate is too soluble in water to be precipitated by ammonium bicarbonate.

It has been made by electrolysis of potassium chloride solution and treatment of the caustic potash obtained with carbon dioxide. Much potassium carbonate is made by treating potassium chloride with magnesium carbonate and carbon dioxide, when an insoluble magnesium potassium hydrogen carbonate results.

$$3MgCO_3 + 2KCl + CO_2 + 9H_2O \rightarrow 2(MgKH(CO_3)_2 \cdot 4H_2O) + MgCl_2.$$

This, when treated with hot water, yields insoluble magnesium carbonate and a solution of potassium carbonate,

$$2[MgKH(CO_3)_2 \cdot 4H_2O] . = 2MgCO_3 + K_2CO_3 + CO_2 + 9H_2O.$$

The Leblanc process (§ 235), can be and is applied to the manufacture of potassium carbonate from potassium chloride. The only notable difference from the process as used for manufacturing soda

is that the salt produced is not crystallised out from the liquors obtained by extracting the black ash with water. These liquors are, instead, evaporated to dryness.

Potassium carbonate is obtained from various vegetable products, notably wood ashes. The ashes contain up to 15 per cent. of potassium carbonate. They are extracted with water and the liquors so obtained are boiled dry. A certain amount of potash is made from the residues remaining when beet-sugar is crystallised from the beet-juice. Potash has also been recovered from 'suint,' the sweat, etc., which forms some 30 per cent. of the weight of raw wool, and which is washed out before the wool is used.

*Properties.*—Potassium carbonate is a white substance, melting at about 880° C. It is deliquescent and is exceedingly soluble in water, 100 gms. of which dissolve 109 gms. of the carbonate at 15° C. and 156 gms. at 100° C. Unlike sodium carbonate, it does not form any stable hydrates.

It finds some use as a dehydrating agent. Thus, if alcohol containing some water be shaken with solid potassium carbonate, the latter dissolves in the water, forming an oily layer on which floats the alcohol, freed from much of its water.

In its chemical properties it resembles sodium carbonate.

*Uses.*—Potassium carbonate finds a use in industry in the manufacture of soft soap, which consists of potassium compounds of the organic acids contained in fats and oils. Ordinary soap is the sodium compound. It is also used in the manufacture of hard glass (§ 600), and of the numerous potassium salts used in the chemical industry.

**263. Potassium Nitrate, Nitre, Saltpetre, $KNO_3$.**—Potassium nitrate has been known since the eighth century A.D. The 'nitre' of the Bible is 'natron,' native sodium carbonate. Nitre was manufactured up to the latter part of last century from saltpetre earth by methods which are still used locally on a small scale in the East.

*Manufacture from Saltpetre Earth.*—In the neighbourhood of Indian villages the ground becomes saturated with the nitrogenous compounds contained in crude sewage. Certain bacteria (§ 674) 'nitrify' these, *i.e.*, convert them to nitrates. The soil is removed and extracted with water and by crystallisation a very impure potassium nitrate, containing a good deal of common salt, is obtained. This product may be recrystallised.

*Manufacture from Sodium Nitrate.*—Most of the world's saltpetre is made by the action of the Stassfurt potassium chloride on Chilean sodium nitrate. These salts, when mixed in solution, give four different ions, $Na^+$, $K^+$, $Cl^-$, $NO^-_3$, which by their various combinations, can give four different salts. The particular salts formed depend upon the solubilities of these compounds under the conditions prevailing.

The solubilities of the four salts concerned are as given in the table below.

It follows then that if boiling saturated solutions of potassium chloride and sodium nitrate react, the least soluble salt present in the boiling equilibrium mixture will be sodium chloride, and this will separate out. If now, the liquid is filtered while hot and allowed to cool to 20° C. or under, potassium nitrate becomes the least soluble salt and crystallises out. The sodium chloride having largely deposited from the hot solutions and being but little less soluble in the cold solution, does not deposit and contaminate the product.

| | 100 gms. water dissolve. | |
|---|---|---|
| | At 20 °C. | At 100 °C. |
| Sodium nitrate . . . . | 87·5 | 180 |
| Potassium chloride . . . | 37·4 | 56·6 |
| Sodium chloride . . . . | 35·6 | 40·8 |
| Potassium nitrate . . . . | 31·2 | 247 |

On the laboratory scale potassium nitrate may be made from sodium nitrate by mixing 190 gms. of sodium nitrate, 150 gms. of potassium chloride and 200 c.c. of water. The mixture is boiled, filtered through a hot Buchner funnel and cooled, stirring to avoid the formation of large crystals. The crystals are washed and recrystallised from hot water.

Potassium nitrate forms white crystals, easily soluble in hot water but much less soluble in cold. Its solubility curve is given in Fig. 23.

When heated, potassium nitrate melts at 340° C., and then decomposes slowly, giving oxygen and the nitrite

$$2KNO_3 = 2KNO_2 + O_2.$$

It has the usual properties of a nitrate (§ 750).

The chief use of potassium nitrate is in the manufacture of fireworks and gunpowder. The latter is a mixture containing approximately 6 parts of potassium nitrate, 1 of charcoal and 1 of sulphur. These are ground very finely in the moist state and slowly dried. The powder, when ignited, burns almost instantaneously, producing a great quantity of gas, mainly nitrogen and oxides of carbon, the expansion of which provides the propellant or disruptive force of the powder. A solid 'fouling' is left behind, containing potassium sulphide and carbonate.

*Potassium nitrite* $KNO_2$ resembles sodium nitrite, but is even more soluble, 100 gms. of water dissolving no less than 300 gms. of the salt at 15·5° C.

**264. Potassium Salts of the Acids of Sulphur.**—*Potassium sulphides.*—These resemble the sulphides of sodium (§ 244), and are prepared by similar methods. The action of potassium carbonate on an excess of sulphur yields mainly the pentasulphide $K_2S_5$. This product is known as 'liver of sulphur.'

*Potassium sulphate* $K_2SO_4$.—This salt is usually made by the action of sulphuric acid upon potassium chloride (cf. sodium sulphate, § 246). It is also prepared from the mineral kainite $K_2SO_4 . MgSO_4 . MgCl_2 . 6H_2O$. This is crystallised in much the same way as carnallite (§ 265), when *schoenite*, potassium magnesium sulphate $K_2SO_4 . MgSO_4 . 6H_2O$ crystallises out. A hot solution of this is then treated with solid potassium chloride, when the reaction

$$K_2SO_4 . MgSO_4 + 3KCl = 2K_2SO_4 + KCl . MgCl_2$$

takes place. The potassium sulphate crystallises out at temperatures above 40° C. Below this temperature other salts crystallise.

Potassium sulphate forms colourless, rhombic crystals. It is somewhat sparingly soluble in water, 100 gms. of which dissolve 11·11 gms. of the salt at 20° C. and 24·1 gms. at 100° C. It differs from sodium sulphate in that it forms no hydrates, but in other respects resembles that salt.

*Potassium hydrogen sulphate* $KHSO_4$ resembles the sodium salt in most respects.

*Potassium persulphate* is discussed in § 946.

**265. Potassium Chloride KCl.**—Potassium chloride is found native as *sylvine* KCl, and *carnallite* $KCl . MgCl_2 . 6H_2O$. These minerals are found in the salt deposits of Stassfurt. They occur as a deposit at a higher level than the main mass of rock salt and probably represent the product of the final drying up of an inland sea, the most soluble of the salts contained in the water being deposited last and at the highest level.

The extraction of potassium chloride from carnallite is carried on in the manner described below.

Carnallite $KCl . MgCl_2 . 6H_2O$ is decomposed in presence of water and is only stable in presence of a solution containing much magnesium chloride. When it is treated with a small quantity of water potassium chloride separates out and magnesium chloride goes into solution. On heating, the potassium chloride dissolves and the solution, when cooled, deposits the salt in crystals large enough to be separated.

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The carnallite is crushed coarsely and is placed in a tank fitted with a false bottom, where it is mixed with the mother liquors resulting from the washing of the potassium chloride crystals produced in a previous operation.

The mixture is agitated and boiled by injecting steam, and then is allowed to stand until the mud, etc., has settled out. The clear liquor, containing potassium and magnesium chlorides, is drawn off and allowed to cool slowly for two or three days in tanks holding some 200 or more cubic feet. The resulting crystals contain some 25 per cent. of sodium chloride and are purified by careful washing with a little water. The salt still retains some sodium chloride, and ihis can be separated by further recrystallisation.

A certain amount of potassium chloride is now recovered from the water of the Dead Sea.

Potassium chloride forms white cubic crystals similar to those of sodium chloride, which salt it resembles in almost all particulars. It is, however, more fusible (M.P. 770° C.). Potassium chloride is more soluble than sodium chloride in hot water, but is less soluble in cold (27·6 gms. in 100 gms. water at 0° C., 56·7 at 100° C.).

**266. Other Halogen Compounds of Potassium.** — *Potassium chlorate* $KClO_3$ and *Potassium perchlorate* $KClO_4$ are discussed in §§ 1071, 1072.

*Potassium bromide* KBr.—This salt can be prepared in the laboratory by the action of bromine on warm strong caustic potash solution,

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O.$$

The solution is evaporated to dryness and ignited with a little charcoal, which reduces the bromate to bromide,

$$2KBrO_3 + 3C = 2KBr + 3CO_2.$$

The mass is then recrystallised.

On the commercial scale iron bromide is first prepared by the action of iron borings on bromine,

$$3Fe + 4Br_2 = Fe_3Br_8.$$

The solution of this salt is then run into potassium carbonate solution until the solution is neutral,

$$Fe_3Br_8 + 4K_2CO_3 + 4H_2O = 8KBr + 2Fe(OH)_3 + Fe(OH)_2 + 4CO_2.$$

The solution of the bromide is filtered from iron hydroxides and crystallised.

Potassium bromide forms white cubic crystals readily soluble in water (65 gms. per 100 gms. water at 20° C.).

Its properties are discussed in § 1081. Potassium bromide forms unstable compounds with bromine, $KBr_3$ and $KBr_5$. Thus bromine dissolves freely in a solution of potassium bromide.

Potassium bromide is used in medicine as a sedative, and in photographic developers as a "restrainer."

*Potassium iodide* KI is made by a process very similar to that used for the bromide.

It forms white cubic crystals very soluble in water, 100 gms. of which dissolve 144 gms. of the salt at 20° C., and 208 gms. at 100° C.

Its properties are discussed in §§ 1096, 1097. Solutions of potassium iodide dissolve iodine to a considerable extent, the salt $KI_3$ (cf. § 271, 1089) being formed in solution. The compounds $KI_3 . H_2O$ and $KI_7 . H_2O$ have been isolated in the solid state, but these polyiodides do not appear to exist except in combination with water. Polyhalides of rubidium and cæsium (§ 271) exist in the solid state and uncombined with water.

**267. Tests for Potassium and Sodium.**—*Detection.*—A solution of the substance to be tested is treated with ammonium hydroxide and ammonium carbonate and the compounds of the metals other than the alkali metals and magnesium are precipitated as carbonates or hydroxides and filtered off.

Magnesium is tested for in the filtrate by means of sodium phosphate, and, if present, is removed as hydroxide by addition of barium hydroxide, excess of which is then removed by addition of sulphuric acid.

The solution is then evaporated to dryness and the residue heated strongly to volatilise all ammonium salts. It is then taken up in a little water and portions are tested for potassium in one of the following manners, which are here set down in order of preference :—

(1) Hexachlorplatinic acid (platinum tetrachloride) is added and then an equal volume of alcohol. A yellow precipitate of potassium hexachlorplatinate $K_2PtCl_6$ indicates the presence of the metal.

(2) A solution of perchloric acid (20 per cent.) is a much cheaper reagent. If a solution of a potassium salt is mixed with such a solution and an equal volume of alcohol, white potassium perchlorate is precipitated.

(3) A solution of sodium cobaltinitrite gives a yellow precipitate of potassium cobaltinitrite (§ 1192). This is a comparatively delicate test.

(4) A solution of sodium picrate precipitates yellow crystalline potassium picrate from solutions of potassium salts. A precipitate is also given by sodium carbonate, and the absence of this salt should be ensured by careful neutralisation.

(5) A solution of tartaric acid, when added to a not too dilute solution of a potassium salt, precipitates potassium hydrogen tartrate $KHC_4H_4O_6$. The test is less delicate than the others.

(6) The flame test may be applied to the residue. A little sodium will obscure the flame colour of a potassium salt, but if the flame is viewed through blue glass the lilac colour is readily seen. The use

of a direct-vision spectroscope enables the lines of the potassium spectra in the blue and red to be seen even when sodium is present. The test is less reliable than the precipitation reactions. It is necessary to remove the heavy metals before applying the test, as some of these give colours not unlike that given by potassium.

Sodium may be detected by the flame test as described above, but owing to the very strong colour given to the flame by the salts of this element, care should be taken that an accidental trace of sodium does not obscure the colour given by a much larger quantity of potassium.

The solution, freed as above from all metals except the alkali metals, may also be tested for sodium by one of the following procedures :—

(1) The solution is evaporated to dryness and the solid heated to strong redness to remove ammonium salts, etc., then taken up in a little water. To the solution is added potassium pyroantimonate solution (§ 820) and the liquid allowed to stand. A white *crystalline* precipitate of sodium pyroantimonate indicates the presence of sodium. The pyroantimonate solution is made by boiling 20 gms. of the salt with a litre of water till nearly all has dissolved. The solution is cooled quickly and a little caustic potash added. It is then filtered and used.

(2) To a fairly strong solution of the sodium salt made as above a solution containing nickel acetate and uranyl acetate is added. A yellow precipitate of sodium nickel uranyl acetate indicates the presence of sodium.

Sodium and potassium are commonly estimated as sulphate. Other metals are removed as described above and the solution, containing only sodium or potassium, is evaporated with sulphuric acid in a platinum basin. The residue is heated until no further change in weight occurs, when the metal may be weighed as the pure anhydrous normal sulphate.

$$NaX + H_2SO_4 = NaHSO_4 + HX$$
$$2NaHSO_4 = Na_2SO_4 + H_2SO_4.$$

Potassium may also be estimated as platinichloride (*v. supra*).

## RUBIDIUM Rb, 85·48

**268. Occurrence and Discovery of Rubidium.**—Rubidium was discovered by Bunsen and Kirchhoff in 1861, in a mineral water, by spectroscopic examination. Two dark-red lines were found in the spectrum and these were assigned to an element named by them rubidium (*rubidus*, dark-red).

Rubidium is an extremely rare element occurring to the extent of some 1 per cent. in the mineral lepidolite. It occurs also in the Stassfurt deposits, and is extracted from the mother liquors obtained in the extraction of potassium chloride (§ 265).

**269. Properties of Rubidium and Its Compounds.**—Rubidium bears the closest resemblance to potassium. It is softer and more fusible and volatile (M.P., 38° C.; B.P., 696° C.). It is heavier than water. Its reactions resemble those of potassium but are more vigorous.

Its compounds resemble those of potassium, differing only in density, solubility and minor properties.

Its salts colour the Bunsen flame reddish violet.

## CÆSIUM Cs, 132·91

**270. Occurrence and Discovery.**—Cæsium was discovered at the same time and in the same manner as rubidium. It gives two lines in the blue of the spectrum. Cæsium occurs with rubidium in small quantities in lepidolite and also in the rare mineral pollucite, cæsium aluminium silicate, which contains up to 30 per cent. of cæsium.

**271. Properties of Cæsium and Its Compounds.**—In its physical and chemical properties cæsium resembles rubidium. It is softer, more fusible, more volatile, and denser than the latter (M.P., 28° C.; B.P., 670° C., D., 1·9.)

Cæsium is even more reactive than rubidium, but otherwise resembles that metal, in its chemical properties.

Cæsium compounds are for the most part very soluble in water, the chloride, sulphate and iodide all dissolving in less than their own weight of water at room temperature.

The monoxide $Cs_2O$ is interesting as being scarlet in colour.

Both cæsium and rubidium differ from the other alkali metals in forming stable polyhalides. Compounds of the types $M'I_3$, $M'Br_3$, $M'IBr_2$, $M'ICl_2$, $M'BrCl_2$, $M'IFBr$, $M'FICl_3$, exist in the solid state, though they readily lose halogen when heated. The metal is not tri- or quinque-valent, for these salts may be considered as derived from complex acids of the type $HI_3$, etc., some of which have been isolated.

## FRANCIUM Fr

An element of atomic number 87 and atomic weight 223 has been identified in the products of the radioactive decay of actinium. Its half-period is 21 min. and it cannot therefore be isolated.

# CHAPTER XI

## COPPER—SILVER—GOLD

**272. Properties and Electronic Structure of Group I. B.**—Copper, silver and gold are transition elements, included in the first group of the periodic table, but not closely resembling Group I. A, the alkali metals. The numbers of electrons at the various levels of the copper atom are 2 . 8 . 18 . 1 ; while those of the electrons in the potassium atom (an alkali metal) are 2 . 8 . 8 . 1. The distinguishing feature is that the copper atom has a shell of eighteen electrons immediately below the outer valency electron, and that this shell is not so stable that another electron cannot be withdrawn from this level for valency purposes. The loss of the single outer electron of the potassium atom leaves a structure of 'inert-gas' type, and from the potassium atom only one electron can be removed. The removal of one or two outer electrons from the copper atom does not leave a structure of 'inert-gas' type, and so is unaccompanied by great changes in stability and energy. Copper compounds are much less stable than potassium compounds, and the copper ions are much more readily reducible than those of, say, potassium.

The same considerations apply, still more strongly, to silver and gold.

Thus we find that the metals of Group I. B. are remarkably resistant to chemical attack. They are less electropositive than hydrogen, and are therefore unattacked by acids in general. Only strong oxidising agents and substances which form complex ions with them are effective in attacking the metals.

Their compounds are unstable. Their oxides are decomposed by heat—cupric oxide with difficulty, silver and gold oxides very easily.

The salts of copper are fairly stable, those of silver less so, while gold salts are all readily decomposed by the action of heat. The tendency to formation of complex ions is as notable in this group as it is absent in Group I. A. Among copper compounds we may note chlorocuprous acid (§ 288), the cuprammonium compounds and the cuprocyanides. Similar compounds of silver and gold exist, and are even more stable than those of copper.

We shall find, then, that the group is distinguished by the slight reactivity of the elements and the ready decomposition of the

compounds—these features being least marked in copper and most marked in gold.

## COPPER Cu, 63·57

**273. Historical.**—Copper is, after gold, the most anciently known metal, and its use coincides with the dawn of history. The reason for the early discovery of gold, silver and copper is the readiness with which their compounds are decomposed. Gold compounds are so unstable that the metal is found native, while silver and copper are so easily won from their ores that their early discovery was inevitable. The minerals of copper are conspicuous—brilliant green malachite and brassy pyrites—and the metal is easily obtained by simply building a fire of charcoal and malachite in lumps. The copper would be formed by the reactions

$$CuCO_3 = CuO + CO_2$$
$$2CuO + C = 2Cu + CO_2,$$

and would melt and flow to the bottom of the fire.

Rich copper pyrites can also be smelted in the same simple way.

In classical times, copper was used chiefly as bronze, a copper-tin alloy containing some 12 per cent. of the latter element. Many compounds of copper were also known.

Burnt copper, '*æs ustum*,' was probably cuprous oxide, used as a pigment. Black oxide of copper was known, as also was verdigris, and crude copper sulphate, *chalcanthum*.

**274. Sources of Copper.**—Copper is found as native copper in the Lake Superior district, but the chief ore of copper is *chalcopyrite*, or *copper pyrites*, $Cu_2S \cdot Fe_2S_3$ or $CuFeS_2$. This is not as a rule found pure, but mixed with much iron pyrites, $FeS_2$. Other ores occasionally worked are *malachite*, $CuCO_3 \cdot Cu(OH)_2$; *azurite*, $2CuCO_3 \cdot Cu(OH)_2$; *atacamite*, $CuCl_2 \cdot 3Cu(OH)_2$; *bornite*, $Cu_2S \cdot CuS \cdot FeS$; *chrysocolla*, $CuSiO_3 \cdot 2H_2O$; *fahlore*, copper and silver sulpharsenites and sulphantimonites. Among the less common minerals of copper are *chalcocite*, cuprous sulphide $Cu_2S$; *cuprite*, cuprous oxide $Cu_2O$; *melaconite*, cupric oxide CuO.

**275. Manufacture of Copper by Smelting.**—Copper is to-day chiefly obtained from pyritic ores consisting of iron and copper sulphides.

If the copper exceeds 4 per cent., smelting is employed. For very poor ores containing less than this proportion the cementation process is used.

There are several varieties of process in use for smelting copper, but the commonest of them is that of :—

(1) Roasting the ore to remove the arsenic and much of the sulphur.

(2) Reducing the *matte* so obtained in Bessemer converters.
(3) Refining the copper so produced.

The first process is performed in many different ways, but preferably by *pyritic smelting*. The copper ore is charged into a blast furnace together with a very little coke and some free silica (quartz, sand, etc.). The combustion of the ore itself provides the heat and so no fuel is needed, a great boon in many copper-producing countries, where coal is scarce. The reactions which take place are :—

$$2CuFeS_2 + O_2 = Cu_2S + 2FeS + SO_2$$
$$2FeS + 2SiO_2 + 3O_2 = 2FeSiO_3 + 2SO_2.$$

The cupric sulphide is converted into cuprous sulphide and the ferrous sulphide into ferrous oxide, which, with the silica present, at once forms the silicate. The fused cuprous sulphide mixed with some ferrous sulphide forms a lower liquid layer—the matte—while the fused iron silicate floats above it as a slag.

The matte is usually refined in a Bessemer converter (Fig. 189). This is a vessel of steel plate lined with a thick layer of some material consisting chiefly of silica. It is provided with an entry for an air blast below and an exit above for the gases produced. The red-hot liquid matte is run into the converter and a blast of air blown through it. Oxidation takes place with the production of much heat and the

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$
$$Cu_2S + 2Cu_2O = 6Cu + SO_2,$$

cuprous sulphide reacts with the cuprous oxide so produced, forming copper and sulphur dioxide.

The iron sulphide still remaining is oxidised to oxide and this combines with the siliceous lining of the converter to form ferrous silicate which forms a liquid slag. The slag is first poured off by tipping the converter, and the copper is then poured into moulds.

Copper so made contains some sulphide and also gold and silver in small quantities, together with traces of other impurities, including lead, arsenic, nickel, antimony, zinc, iron, cobalt, bismuth, tin, etc.

**276. Refining of Copper.**—For most purposes, and especially for electrical conductors, copper is required in a high state of purity. The metal is refined by two methods. The first consists of furnace treatment, the second is electrolytic.

By the first method the copper is melted in a reverberatory furnace (Fig. 188), where it is exposed to an oxidising atmosphere. The impurities, gold and silver excepted, are oxidised and either volatilised or converted into slag. The copper thus purified contains a little cuprous oxide which diminishes its toughness. This is

removed by holding poles of green wood beneath the liquid metal. The reducing gases, methane, etc., given off convert the cuprous oxide into copper.

If copper of very high purity is required or if gold and silver are contained in it in sufficient quantities to be worth recovering, it is refined by *electrolysis*. To this end a slab of impure copper is made the *anode*, and a sheet of pure copper the *cathode*, in an electrolytic cell, in which the liquid is copper sulphate solution.

The cupric ion travels to the cathode sheet and is deposited thereon, while the anode is converted into cupric ion,

$$\text{Cathode} \quad Cu^{++} + 2\ominus = Cu$$
$$\text{Anode} \quad Cu = Cu^{++} + 2\ominus.$$

Any gold and silver contained in the copper are not converted into ions but sink to the bottom as a 'slime' of finely-divided metal. As one copper atom is deposited on the cathode and one taken from the anode for every two electrons that pass, the quantity of copper sulphate in the solution remains unchanged.

**277. The Cementation Process.**—Very poor ores of copper, of which great quantities are to be found, are treated by the cementation process. The ore is heaped up into vast embankments containing four or five million tons of ore, and water is allowed to percolate through and over it. Copper sulphide is more easily oxidisable than iron sulphide and slowly reacts with air and water, forming copper sulphate. Some iron sulphate and sulphuric acid are also formed,

$$CuS + 2O_2 = CuSO_4,$$
$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4.$$

The liquid flowing from the bottom of the heaps is pale green in colour and contains a proportion of copper sulphate and ferrous sulphate. The liquid is then allowed to flow through concrete channels containing scrap iron. Here the reaction,

$$Fe + Cu^{++} = Fe^{++} + Cu$$

takes place and the iron dissolves, being replaced by a dark friable deposit of metallic copper. This is dug out, roughly dried and refined by melting and poling as described above.

**278. Properties of Metallic Copper.**—Copper is a solid of metallic lustre and a salmon-pink colour. The darker tint of ordinary copper is the result of a film of sulphide or oxide. Copper melts at 1,083° C; its specific gravity is 8·95. Its specific heat at 20° C. is 0·0915. Copper has a high conductivity both for heat and electricity; its specific resistance is $1{\cdot}78 \times 10^{-6}$ at 18° C. The liquid metal is

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miscible with most other liquid metals, forming alloys, which are discussed below.

Copper does not burn in air, but when heated to redness forms first cuprous oxide $Cu_2O$, and then cupric oxide CuO. It burns, if finely divided or in thin sheets, in chlorine and in sulphur vapour.

Copper is attacked by steam only at a white heat. Copper is less electropositive than hydrogen and is, therefore, not attacked by such acids as are not also oxidising agents.

The reaction of a metal with an acid is supposed to depend on an equilibrium such as

$$Cu + H^+ \rightleftharpoons Cu^+ + H.$$

The equilibrium constant is given by

$$K = \frac{[Cu^+]\,[H]}{[Cu]\,[H^+]}$$

The concentration of copper is constant; it follows that a decrease of the concentration of cuprous ion ($Cu^+$) will cause an increase of [H], and a decrease of [$H^+$], or, in other words, it will cause the acid to evolve hydrogen and the copper to dissolve.

If the copper dissolved to $Cu^+$ as it would with, say, dilute sulphuric or hydrochloric acid, [$Cu^+$] would at once rise and [H] would fall below the solubility of hydrogen, for K is (for copper) very small. The action would therefore instantly cease.

With nitric acid the hydrogen is oxidised to water; accordingly [H] is negligible, and an appreciable concentration of $Cu^+$ (actually oxidised to $Cu^{++}$) may be formed.

With hydrobromic acid the $Cu^+$ ion is almost wholly removed in consequence of the reaction

$$2Cu^+ + 4Br^- \rightleftharpoons [Cu_2Br_4]^{--}$$

Thus the concentration of $Cu^+$ ion is kept so low that [H] becomes high enough for hydrogen to be evolved. Hydriodic acid reacts similarly. Thus, a metal which does not react with ordinary acids will be likely to react with such acids (1) as oxidise hydrogen to water, (2) as form a complex ion with the ion of the metal.

In presence of air copper is slowly attacked by many acids, the process being:

$$2Cu + O_2 = 2CuO$$
$$CuO + 2H\bar{A} = Cu\bar{A}_2 + H_2O.$$

Examples are the formation of basic copper carbonate, of verdigris and of copper sulphate by the commercial method.

Copper exposed to air and moisture becomes covered with a beautiful green coating. It has recently been shown that this is not the basic carbonate, as formerly believed. In inland districts the basic sulphate, *brochantite*, $CuSO_4 \cdot 3Cu(OH)_2$, or near the sea, the basic chloride, *atacamite*, $CuCl_2 \cdot 3Cu(OH)_2$, constitute this coating.

With nitric acid copper reacts vigorously, producing copper nitrate and nitric oxide with a large or small proportion of nitrogen peroxide. The reactions may be summed up as :

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$
$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2.$$

The last reaction occurs chiefly with concentrated acid. For the mechanism of these reactions, see § 744.

With dilute sulphuric acid copper does not react unless air is present, when copper sulphate (*q.v.*) is slowly formed,

$$2Cu + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O.$$

The concentrated acid forms copper sulphate and sulphur dioxide and also some copper sulphide.

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

These reactions are further discussed in § 936. Copper is not attacked by alkalis.

Copper being near the electronegative end of the electrochemical series of metals (§ 126), is displaced from its salts by most other metals. In fact, copper ion is reduced to copper by all metals, except gold, silver and the platinum metals,

$$Zn + Cu^{++} = Zn^{++} + Cu.$$

Copper displaces silver and the other metals mentioned above from their salts.

$$Cu + 2Ag^{+} = Cu^{++} + 2Ag$$

*or*

$$Cu + 2AgNO_3 = Cu(NO_3)_2 + 2Ag.$$

If a copper wire be immersed in dilute silver nitrate solution a beautifully crystalline "silver-tree" is formed.

**279. Alloys of Copper.**—These are numerous and may with advantage be tabulated :—

PERCENTAGE COMPOSITION OF COPPER ALLOYS.

| Alloy. | Copper. | Tin. | Zinc. | Lead. | Iron. | Nickel. |
|---|---|---|---|---|---|---|
| Bronze . . . | 75–90 | 25–10 | | | | |
| Brass . . . | 70–80 | — | 30–20 | | | |
| Delta metal . . | 60 | — | 38·2 | — | 1·8 | |
| Monel metal [1] . . | 27 | — | — | — | 2–3 | 68 |
| German silver . . | 25–50 | — | 35–25 | — | — | 35–10 |

[1] Traces of Mn, C, S, also present up to c. 2 per cent.

*Bronze* is distinguished by its toughness and great tenacity. It is peculiarly suitable for parts of machinery which must withstand great shocks without breaking, such as the propellers of ships.

*Phosphor bronze* (Cu, 95 per cent. ; Sn, 5 per cent. ; P, 0·05 per cent.) is a fatigue-resisting alloy and is therefore used in operations where resistance to alternating or cyclic stresses is required, as in ship's propellers. Copper alloys containing beryllium are rapidly becoming important. The alloy, Cu 97·75 per cent., Be 2·25 per cent., develops a strength six times that of commercial copper on heat treatment, with a much smaller loss of electrical conductivity than results from the addition of other hardening agents such as Si, Sn. P. It is used where a combination of these qualities are required, as in current-carrying springs.

*Brass* finds its chief uses as a result of its ornamental colour and the ease with which it can be turned on the lathe, pressed into shape, etc. When it contains a low proportion of zinc it is softer and richer in colour. With more zinc it becomes harder, paler yellow and more brittle.

*Delta metal* is a brass containing iron and is extremely tenacious, having nearly as great a breaking strain as the strongest steel.

*Monel metal* is a copper-nickel alloy of great strength and very resistant to chemical action. It finds considerable use in the chemical industries.

*German silver* is a white metal of variable composition containing as a rule, copper, zinc and nickel. Its properties resemble those of brass.

*Coinage Alloys.*—The so-called copper coins are alloys of copper and tin containing 7·5 per cent. of the latter metal. The English silver coins formerly consisted of an alloy of 92·5 per cent. silver and 7·5 per cent. copper. The modern coins contain but 50 per cent. silver, the remainder consisting of 40 per cent. copper and 5 per cent. each of zinc and nickel.

Copper containing 0·25–0·50 per cent. arsenic has a high resistance to corrosion and erosion, whilst it has a much higher annealing-temperature than the pure metal. It is used therefore in locomotive fire-boxes and in the radiators of motor vehicles.

**280. Atomic Weight of Copper.**—An approximate value of 64 fits in with Dulong and Petit's law and the periodic system. The exact atomic weight has been obtained by various methods, amongst which may be mentioned :—

(1) The conversion of copper sulphate into barium sulphate, giving the ratio, $CuSO_4 : BaSO_4$.

(2) The conversion of cupric bromide into silver bromide.

(3) The determination of the *electro-chemical* equivalent by passing a current of electricity through two cells, arranged in series, one

containing a copper salt and the other containing a silver salt. According to Faraday's law (§ 114) the weights of the two elements deposited on the cathodes should be in the proportion of their chemical equivalents. This method gives the result that for every 107·883 gms. of silver (1 equivalent) there is deposited 31·78 gms. of copper, which is therefore the gram-equivalent of that metal. The atomic weight is therefore twice that value, 63·56, fitting in with the approximate figure given above.

The best value appears to be 63·57.

*Isotopes of Copper.*—Copper consists of two isotopes (§ 148) of atomic weight 63·0 and 65·0 in the proportion of about 2 : 5.

**281. Oxides of Copper.**—There appear to be three undoubted oxides of copper, of which only two are of any importance. Two lower oxides, $Cu_3O$ and $Cu_4O$, have been described, but their chemical individuality is doubtful.

| | |
|---|---|
| Cuprous oxide | $Cu_2O$. |
| Cupric oxide | $CuO$. |
| Copper peroxide hydrate | $CuO_2(OH)_2$. |

**282. Cuprous Oxide.**—Cuprous oxide is not usually prepared by the usual methods for making oxides. It may be made—

(1) By heating cupric oxide with copper powder,

$$Cu + CuO = Cu_2O.$$

(2) By reducing a cupric salt with glucose, in presence of alkali. The usual laboratory method of preparation is given below.

Dissolve 10 gms. of crystallised copper sulphate and 15 gms. Rochelle salt (sodium potassium tartrate) in 75 c.c. of water and gradually add 15 gms. caustic soda, dissolved in 25 c.c. of water, stirring well. Add to the resultant solution 20 gms. of glucose and boil for some time. When the blue colour has nearly, but not quite, disappeared, allow the red cuprous oxide to settle, wash by decantation with hot water, filter by suction. Wash well on the filter and dry in the steam oven.

*Properties of Cuprous Oxide.*—Cuprous oxide is insoluble in water. It occurs in yellow and red forms, differing only in size of particles. When heated in air it is slightly oxidised, forming cupric oxide, and when heated in hydrogen it is reduced to copper.

Acids react with it in a peculiar manner. In most cases cuprous salts are not formed, as might be expected, but instead a mixture of a cupric salt and copper is produced (§ 289a).

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$

Hydrochloric acid, however, reacts with it to form cuprous chloride, which dissolves in the acid, forming chlorocuprous acid $H_2Cu_2Cl_4$,

$$Cu_2O + 2HCl = Cu_2Cl_2 + H_2O.$$

Nitric acid reacts violently with it, giving cupric nitrate and oxides of nitrogen. Cuprous oxide gives a deep red colour to glass, and this is its chief industrial use. The red colour is probably due to the presence of minute particles of metallic copper.

**283. Cupric Oxide, Black Oxide of Copper, CuO.**—This oxide can be made by all the usual methods for preparing oxides. It is usual to prepare it on the commercial scale by heating malachite, native copper carbonate,

$$CuCO_3 . Cu(OH)_2 = 2CuO + H_2O + CO_2.$$

It is also made from copper scale, the scourings of copper sheets, obtained when copper is being worked. This material, which consists mainly of crude copper oxide, is moistened with nitric acid to remove cuprous oxide or metallic copper, and heated to redness to convert the nitrate so formed into oxide.

In the laboratory it may be prepared by heating the nitrate, carbonate, or hydroxide of the metal.

Copper oxide is a black powder, insoluble in water, but definitely hygroscopic. When very strongly heated it decomposes, giving cuprous oxide at about 1,000° to 1,200° C.

It has the usual properties of a basic oxide, forming salts with all acids.

The oxide is readily reduced to metal in a current of hydrogen or by heating with carbon,

$$CuO + H_2 = Cu + H_2O,$$

or organic substances. The chief method of ultimate organic analysis depends on the fact that the organic substances react with heated copper oxide to form carbon dioxide and water, which are easily absorbed and weighed,

$$C_nH_mO_p + \left(2n + \frac{m}{2} - p\right) CuO$$

$$= nCO_2 + \frac{m}{2}H_2O + \left(2n + \frac{m}{2} - p\right) Cu.$$

Copper oxide is used chiefly for colouring glazes and glasses green or blue. The colour is due to copper silicate.

**284. Copper Peroxide $CuO_2(OH)_2$** is obtained by the action of hydrogen peroxide on a neutral suspension of cupric hydroxide at 0° C.,

$$Cu(OH)_2 + 2H_2O_2 = CuO_2(OH)_2 + 2H_2O.$$

It is a yellow-brown powder very readily decomposed when heated to about 180° C.,

$$2CuO_2 = 2CuO + O_2,$$

forming cupric oxide.

## 285. Hydroxides of Copper

*Cuprous Hydroxide* does not appear to exist. The yellow precipitate obtained when preparing cuprous oxide seems to be a colloidal combination of cuprous oxide and water of no definite formula.

*Cupric Hydroxide* $Cu(OH)_2$ is readily prepared by the action of the calculated quantity of alkali on a solution of a cupric salt,

$$CuSO_4 + 2NaOH = Na_2SO_4 + Cu(OH)_2,$$

or

$$Cu^{++} + 2OH^- \rightleftharpoons Cu(OH)_2 \downarrow .$$

It forms a blue precipitate, which may be dried at a low temperature. Cupric hydroxide is decomposed when heated to 100° C., a black substance of composition $4CuO \cdot H_2O$ being produced. Stronger heating produces cupric oxide.

The hydroxide readily dissolves in acids, forming cupric salts. It also dissolves in ammonia to a deep blue solution.

**286. Cuprammonium Compounds.**—Ammonia forms additive compounds —complex ions—with the cupric ion. Cupric hydroxide in presence of water dissolves to a very small extent, and the resultant dissolved hydroxide dissociates almost completely.

$$Cu(OH)_2 \rightleftharpoons Cu(OH)_2 \rightleftharpoons Cu^{++} + 2OH^- \quad . \quad . \quad . \quad . \quad A$$

Solid. Solution.

Ammonia reacts with the copper ion, forming the cuprammonium ion,

$$Cu^{++} + 4NH_3 \rightleftharpoons Cu(NH_3)_4{}^{++} \quad . \quad . \quad . \quad . \quad . \quad B$$

The removal of almost all the cupric ion from the solution upsets the equilibrium of equation A, and accordingly, copper hydroxide dissolves and ionises until the equilibrium is restored. This may not occur till all the cupric hydroxide has dissolved.

The resulting solutions containing the cuprammonium ion are deep blue, and smell of ammonia. They have the curious property of dissolving cellulose to a thick solution which has been used for preparing artificial silk.

The cuprammonium ion forms salts with acidic ions.

Thus, by the action of excess ammonia on copper sulphate, a deep blue solution can be obtained, which on addition of alcohol precipitates deep blue crystals of cuprammonium sulphate,

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4{}^{--}$$

$$Cu^{++} + 4NH_3 \rightleftharpoons Cu(NH_3)_4{}^{++}$$

$$Cu(NH_3)_4{}^{++} + SO_4{}^{--} + 4H_2O = Cu(NH_3)_4SO_4 \cdot 4H_2O.$$

**287. Salts of Copper.**—There are two classes of copper salts, cuprous salts and cupric salts.

The cuprous salts have the general formula CuX or $Cu_2X_2$, and the cupric salts $CuX_2$ where X is a monovalent atom or group.

CUPROUS SALTS

**288. Cuprous Chloride $Cu_2Cl_2$, or CuCl,** the most important of the cuprous salts, is usually prepared by the action of copper on cupric chloride in presence of concentrated hydrochloric acid,

$$Cu + CuCl_2 = Cu_2Cl_2.$$

Cupric chloride may also be reduced by means of zinc dust or sulphur dioxide,

$$2CuCl_2 + Zn = Cu_2Cl_2 + ZnCl_2$$
$$2CuCl_2 + H_2SO_3 + H_2O = Cu_2Cl_2 + 2HCl + H_2SO_4.$$

In the laboratory, cuprous chloride may be prepared by heating 18 gms. of crystallised cupric chloride with 65 c.c. concentrated hydrochloric acid and 10 gms. copper turnings. These are heated on the water bath for about an hour until the green colour has disappeared. The clear solution is then poured into 500 c.c. of water containing a little sulphur dioxide (to avoid oxidation). The white precipitate is washed by decantation with weak sulphur dioxide solution, filtered at the pump and dried by washing with alcohol and ether. (Yield, *c.* 10 gms.)

Another good method is to pass sulphur dioxide through a solution of cupric chloride in concentrated hydrochloric acid. The product is poured into water and treated as above.

Cuprous chloride is a white solid insoluble in water but soluble in hydrochloric acid. A true solution is not formed, but rather a compound hydrochloro-cuprous acid $H_2Cu_2Cl_4$. It melts at 410° C. to form a yellow transparent substance.

Oxidising agents convert cuprous chloride into cupric chloride,

$$Cu_2Cl_2 + 2HCl + O = 2CuCl_2 + H_2O.$$

Cuprous chloride, when dissolved in hydrochloric acid, forms an additive compound with carbon monoxide, from which the carbon monoxide may be again expelled on boiling. The solution, then, affords us a method of separating carbon monoxide from most other gases.

Cuprous chloride reacts with ammonia, dissolving to form a dark-green solution which absorbs carbon monoxide, the compound $Cu_2Cl_2 . 2CO$ being formed ; it also absorbs acetylene forming the red explosive cuprous acetylide (p. 426).

Cuprous chloride gives with alkalis a yellow precipitate of cuprous oxide, which on boiling is converted into a red modification. With hydrogen sulphide it forms black cuprous sulphide $Cu_2S$.

**289. Other Cuprous Compounds.**—*Cuprous iodide* is formed when an iodide is mixed with a cupric salt, cuprous iodide and iodine being precipitated,

$$2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2.$$

The reaction is used for the volumetric determination of copper (§ 296).

*Cuprous sulphate* can be made in absence of water, but is not formed when sulphuric acid acts on cuprous oxide. In presence of water it forms cupric sulphate and copper.

*Cuprous sulphide* $Cu_2S$ is found as an ore of copper. It is formed when copper is heated in sulphur vapour, and is also produced when copper sulphate solution is heated with sodium thiosulphate solution.

*Cuprous nitrate* does not exist free.

The *cuprous ion* is not $Cu_2^{++}$ but $Cu^+$. It breaks up rapidly into cupric ion and copper,

$$2Cu^+ = Cu + Cu^{++}.$$

Thus all soluble cuprous salts decompose in solution in water into cupric salts and copper. Cuprous chloride is apparently soluble in hydrochloric acid but, in fact, it combines with this acid, forming hydrochlorocuprous acid, which forms the $[Cu_2Cl_4]^{--}$ ion, not the $Cu^+$ ion when it dissociates. The cuprous salts find a use in organic chemistry in the Sandmeyer reactions.

**289a. Equilibrium between Cupric and Cuprous Condition.**—The equilibrium equation $2Cu^+ \rightleftharpoons Cu^{++} + Cu$ gives the key to the conditions under which cuprous and cupric salts are formed.

Thus :—

(1) Cuprous salts dissolved in water (*e.g.*, cuprous sulphate) deposit copper and form a cupric salt.

The cuprous salts which are insoluble (*i.e.*, chloride, bromide, iodide, thiocyanate) are stable. They can be dissolved in ammonia or a halogen acid because complex ions ($Cu(NH_3)_4^+$, $Cu_2Br_4^{--}$, etc.) are formed and not $Cu^+$ ion.

(2) A solution of a cupric salt attacks copper, and some cuprous salt is formed. Equilibrium is reached before much cuprous salt is formed, unless the cuprous ion forms a complex ion, as in the formation of cuprous chloride from cupric chloride and copper (§ 288).

$$Cu^{++} + Cu \rightleftharpoons 2Cu^+$$
$$2Cu^+ + 4Cl^- \rightleftharpoons Cu_2Cl_4^{--}$$

(3) Certain ions are reducing agents and reduce cupric salts to cuprous. Thus, if a cupric salt is mixed with an iodide, cuprous iodide is formed

$$Cu^{++} + 2I^- \rightleftharpoons Cu^+ + I^- + I \rightleftharpoons CuI\downarrow + I.$$

This effect also takes place with the cyanide, nitrite, thiocyanate and sulphite. The cupric salts of these can, however, be made in a non-ionised condition ; *i.e.*, as co-ordination compounds with ethylene-diamine. Thus the compound $\begin{matrix} I \\ I \end{matrix}\!\!>\!Cu\!<\!\begin{matrix} NH_2-CH_2 \\ NH_2-CH_2 \end{matrix}$ is quite stable, for the copper is not ionised to $Cu^{++}$ and so is not reduced by the iodide ion.

(4) Cuprous salts which cannot exist in presence of water [(1) above] or at all, are stable when co-ordinated, for the $Cu^+$ ion is not then formed.

Thus the compound of cuprous nitrate with thio-urea, or better, ethylene-thio-urea is stable.

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If the latter compound $CH_2-NH$ / $CH_2-NH$ > S is designated as etu, then the compounds $[Cu(4etu)]NO_3$ and $[Cu(3etu)]_2SO_4$ and some others are stable.

### Cupric Salts

**290. Cupric Ion.**—Many cupric salts are soluble in water and produce the cupric ion $Cu^{++}$.

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}.$$

The cupric ion has characteristic properties, and these are displayed by solutions of all cupric salts.

Cupric ion is blue. It is reduced to copper by all metals except mercury, gold, silver and the platinum metals,

$$Cu^{++} + Zn = Cu + Zn^{++}.$$

The cupric ion gives pale blue copper hydroxide with hydroxyl ion (alkalis),

$$Cu^{++} + 2OH^- \rightleftharpoons Cu(OH)_2 \downarrow .$$

With ammonia it gives the hydroxide, which dissolves in excess, forming cuprammonium ion (§ 286).

With hydrogen sulphide a black precipitate of cupric sulphide is formed,

$$Cu^{++} + S^{--} \rightleftharpoons CuS.$$

With ferrocyanides the chocolate-brown colloidal copper ferrocyanide $Cu_2Fe(CN)_6$ is precipitated.

**290a. Cupric Chloride $CuCl_2$.**—Cupric chloride may be prepared by the action of hydrochloric acid on cupric oxide. Evaporation yields green crystals of the tetrahydrate $CuCl_2 . 4H_2O$.

The anhydrous salt is brown as is also a solution of the salt in concentrated hydrochloric acid. This can be shown to contain an acid $H_2CuCl_4$, and the brown colour is due to $CuCl_4^{--}$ ion. It is therefore thought that anhydrous cupric chloride is an autocomplex and is cupric cuprichloride $Cu[CuCl_4]$.

When the brown solution is diluted it becomes first green, then assumes the pale blue colour typical of cupric ion.

When heated to redness, it gives cuprous chloride and chlorine

$$2CuCl_2 = Cu_2Cl_2 + Cl_2.$$

**291. Copper Carbonate.**—Normal copper carbonate does not exist, but various basic salts are known. The fine green mineral malachite is a basic carbonate, $Cu(OH)_2 . CuCO_3$, as also is the deep blue azurite, $Cu(OH)_2 . 2CuCO_3$.

The copper carbonate usually found in the laboratory is made by the action of sodium carbonate on copper sulphate,

$$2Na_2CO_3 + H_2O + 2CuSO_4 = 2Na_2SO_4 + CuCO_3 \,.\, Cu(OH)_2 + CO_2,$$

or $$2Cu^{++} + 2OH^- + CO_3^{--} = CuCO_3 \,.\, Cu(OH)_2.$$[1]

Copper carbonate is also made on the large scale by similar methods, and is known as *verditer* (to be distinguished from *verdigris*, the basic acetate).

When heated it decomposes at a low temperature, yielding the oxide

$$Cu(OH)_2 \,.\, CuCO_3 = 2CuO + H_2O + CO_2.$$

**292. Acetates of Copper.**—Normal copper acetate $Cu(C_2H_3O_2)_2$ forms deep blue-green crystals. The basic acetate, which has the approximate formula,

$$Cu(OH)_2 \,.\, Cu(C_2H_3O_2)_2,$$

is known as verdigris, and is an important green pigment.

The pigment is made by packing earthenware vessels with alternate layers of ' marcs ' (grape-skins left after the pressing of juice from grapes in the wine factories), and sheets of copper. The marcs ferment, and the alcohol produced is further fermented, forming acetic acid, and the reaction takes place between this, the copper and oxygen,

$$Cu + 2C_2H_4O_2 + O = Cu(C_2H_3O_2)_2 + H_2O.$$

The copper sheets are then removed, packed together on end, exposed to the air, being moistened occasionally with sour wine. The reaction which then takes place may be

$$Cu + Cu(C_2H_3O_2)_2 + H_2O + O = Cu(OH)_2 \,.\, Cu(C_2H_3O_2)_2.$$

**293. Copper Nitrate $Cu(NO_3)_2 \,.\, 3H_2O$.**—Copper nitrate is prepared by the usual methods. It forms dark blue crystals which have the ordinary properties of a nitrate.

**294. Cupric Sulphide CuS** is prepared by the action of hydrogen sulphide on cupric sulphate. It is a black solid insoluble in acids other than nitric acid.

**295. Cupric Sulphate, Copper Sulphate, Blue Vitriol $CuSO_4 \,.\, 5H_2O$.**—Cupric sulphate is the most important salt of copper.

It is prepared on the large scale by heating scrap copper in a reverberatory furnace with sulphur. Cupric sulphide is thus formed. The mass is then heated with access of air, giving a gently oxidising atmosphere, and an impure sulphate is formed,

$$Cu + S = CuS$$
$$CuS + 2O_2 = CuSO_4.$$

The crude copper sulphate is dissolved in dilute sulphuric acid, decanted from insoluble impurities and crystallised.

[1] Sodium carbonate solution contains the $OH^-$ ion (see §§ 121, 239).



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The pure salt may be made by dissolving copper oxide in dilute sulphuric acid,

$$CuO + H_2SO_4 = CuSO_4 + H_2O,$$

and recrystallising as often as may be necessary to remove traces of iron, which is the commonest impurity.

Copper sulphate crystallises as the pentahydrate $CuSO_4 . 5H_2O$, in blue transparent crystals of the triclinic system. They are readily soluble in water, 36·6 parts dissolving in 100 parts of water at 10° C., and 203 parts at 100° C. Copper sulphate forms several hydrates, including $CuSO_4 . 7H_2O$, boothite, isomorphous with ferrous sulphate and $CuSO_4 . 5H_2O$, already mentioned. There exist also hydrates $CuSO_4 . 3H_2O$ and $CuSO_4 . H_2O$. When crystallised copper sulphate is heated it slowly loses water. Only four molecules of water are lost at 100° C., the last being driven off only at about 200° C. The crystallised salt is efflorescent when the air is fairly dry (*v.* §§ 208, 209).

Anhydrous copper sulphate forms a white powder. It readily combines with water, evolving heat, to produce the blue pentahydrate. This change of colour is used as a test for water.

Copper sulphate decomposes at about 340° C. and forms the basic sulphate, which decomposes at higher temperatures, leaving the oxide.

Its chemical properties are comprised for the most part in those of cupric ion (§ 290) and those of a sulphate (§ 938).

Copper sulphate finds numerous uses in industry. Its chief use is as a wash for vines, etc., to kill moulds and other fungi which prey on them. Bordeaux mixture, an example of such a wash, is made by adding 11 parts of lime as milk of lime to 16 parts of copper sulphate contained in 1,000 parts of water. It appears to contain a basic sulphate, $Cu_2(OH)_2SO_4$. Copper sulphate is used as a mordant in dyeing, and also finds considerable use in the manufacture of the green pigments containing copper carbonate (*q.v.*).

**296. Detection and Estimation of Copper.**—Copper salts are easily detected in solution by their blue colour which is intensified by addition of ammonia. The dark brown ferrocyanide is also a characteristic precipitate.

Copper is estimated in several ways. It may be electrolysed on to a weighed platinum dish—an accurate but rather slow process. It may be precipitated, weighed and ignited in the form of sulphide. This method has the inconvenience that the sulphide must be ignited in a current of hydrogen.

Finally, copper is very conveniently determined iodimetrically. The material to be analysed is brought into solution in a known

volume of liquid, and an aliquot part of this solution is added to a considerable excess of potassium iodide and the liberated iodine is titrated with sodium thiosulphate,

$$2CuSO_4 + 4KI = 2K_2SO_4 + 2CuI + I_2,$$

or

$$Cu^{++} + 2I^- = CuI + I.$$

One atom of iodine corresponds to one atom of copper.

## SILVER Ag, 107·88

**297. Silver and Copper.**—Silver differs from copper, first, in its even less electropositive character, secondly, in that it has only one series of salts and is practically always univalent. There are however decided likenesses between the free elements; and silver chloride has points of resemblance to cuprous chloride.

**298. Historical.**—Silver has been known since very early times, but it was probably generally known a considerable time after gold. In Egypt, before the eighteenth dynasty, silver was more valuable than gold. Since that time its price has steadily decreased, and its value has of late years varied between a tenth and a sixtieth of that of gold.

**299. Occurrence.**—Silver is found native and also as sulphide, sulpharsenite, sulphantimonite, and chloride. Lead ores commonly contain a proportion of silver, as do also copper ores.

**300. Manufacture of Silver.**—The chief processes in use to-day are :—

(1) The cyanide process.
(2) The desilverisation of lead.

*Cyanide Process.*—The principle of this method depends on the fact that silver ion forms a complex ion with the cyanide ion, and consequently (*v.* §§ 120, 312), silver compounds will dissolve in solutions of cyanides.

The ore, which consists of silver sulphide mixed with numerous impurities, is stamped or ground to an impalpable slime, which is agitated for hours with sodium cyanide solution. The sodium sulphide formed is oxidised to sulphate by the action of the air, and its removal causes the reaction of the silver sulphide and sodium cyanide to be more nearly complete.

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S,$$

or

$$Ag_2S \rightleftharpoons 2Ag^+ + S^{--}$$
$$2Ag^+ + 4CN^- \rightleftharpoons 2[Ag(CN)_2]^-,$$

The solution containing the sodium argentocyanide is then treated with zinc dust or shavings,

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$$2NaAg(CN)_2 + Zn = 2NaCN + 2Ag + Zn(CN)_2.$$

or
$$2Ag(CN)_3^- \rightleftharpoons 2Ag^+ + 4CN^-,$$
$$2Ag^+ + Zn = Zn^{++} + 2Ag$$

The precipitated silver is then simply filtered off and melted with potassium nitrate in order to oxidise any excess of zinc, etc.

*Recovery of Silver from Lead.*—Lead as prepared from galena usually contains silver up to 2 per cent. The most usual method is *Parkes's Process*, followed by *cupellation*.

The principle of Parkes's process is that when argentiferous lead is melted and some zinc is added, the melted zinc and lead do not mix, but form two liquid layers, the lower being lead containing a little zinc, and the upper zinc containing a little lead. Silver is more soluble in melted zinc than in melted lead, and so passes into the layer of melted zinc. The first portion of the liquid to solidify is the upper layer, containing zinc, silver and some lead, and this portion contains almost the whole of the silver originally present in the lead.

The lead is melted in pots containing some 25 tons, and some zinc is added. The metal is repeatedly skimmed as it cools, and the skimmings, consisting of the above alloy of lead, silver and zinc (mixed with an excess of lead), transferred to a smaller pot. The skimmingsa re then carefully heated in a smaller pot and the less fusible silver-zinc-lead alloy is again separated by a perforated ladle. The alloy is then distilled and the zinc is thus recovered, while a lead-silver alloy remains which is refined by cupellation.

*Cupellation.*—This process, more than 2,000 years old, consists in melting the enriched lead in an oxidising atmosphere on a shallow furnace bed composed of bone ash. The lead is oxidised

$$2Pb + O_2 = 2PbO$$

and the litharge melts and soaks into the porous bone ash. The silver remains behind and the end of the operation is marked by the ' blick ' or sudden brightening of the metal to the lustre of melted silver. The process is often performed in two stages, a preliminary enrichment of the lead and a final production of silver.

*Silver of High Purity.*—Extremely pure silver for laboratory purposes has been made by repeatedly recrystallising silver nitrate, then reducing it to the metal and fusing the resulting silver on a lime block in an atmosphere of hydrogen.

**301. Atomic Weight of Silver.**—The atomic weight of silver is a very important quantity, since it is employed in so many atomic weight determinations.

The evidence for the value is discussed in the section on atomic weights (§ 70). The accepted value is 107·88.

**302. Properties of Metallic Silver.**—Silver is a metal of a beautiful white and lustrous appearance. It is of considerable strength, particularly when alloyed with a little copper, and at the same time very malleable and ductile. It is consequently capable of being chased and hammered into all manner of objects of use and beauty. Pure silver is somewhat soft for ordinary use, and the silver commonly met with contains about 7½ per cent. of copper. It is the best conductor of heat and electricity known. Its melting-point is 961·5° C. It can thus just be melted with an ordinary crucible and Bunsen burner. Its sp. gr. is 10·5, and it is therefore denser than copper but not so dense as lead or gold.

Molten silver dissolves up to twenty-two times its own volume of oxygen, probably forming some silver oxide, and on solidification this is evolved with effervescence, giving a peculiar appearance to the surface of the metal. The phenomenon is known as the 'spitting' of silver.

Silver is a markedly inactive metal. It is not attacked by oxygen. Chlorine converts it slowly into silver chloride,

$$2Ag + Cl_2 = 2AgCl.$$

Bromine and iodine attack the metal in the same way, but still more slowly.

Sulphur converts silver into silver sulphide,

$$2Ag + S = Ag_2S.$$

The blackening of silver coins carried in the same pocket with a piece of indiarubber (vulcanised with sulphur) is due to this reaction. Hydrogen sulphide also blackens silver, and to this cause is due the familiar tarnishing of the metal,

$$2Ag + H_2S = Ag_2S + H_2,$$

Silver is not attacked by acids other than concentrated sulphuric acid and nitric acid of all degrees of dilution, also hydriodic acid.

In the first case silver sulphate and sulphur dioxide are formed,

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2,$$

in the second case silver nitrate and nitric oxide,

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O.$$

Hydriodic acid forms the $AgI_2^-$ ion (*cf.* § 278).

**303. Alloys of Silver.**—For most purposes 'silver' consists of an alloy of 92·5 per cent. silver and 7·5 per cent. copper. Such an alloy is used for British hall-marked plate and, before 1921, was used for British silver coinage. Various other silver-copper alloys are employed in foreign countries. These have a white colour if they contain more than about 40 per cent. of silver.

*The coinage alloy* used in Great Britain at the present date consists of 50 per cent. silver and 50 per cent. of base metal, consisting of copper 40%, nickel 5% and zinc 5%.

**304. Colloidal Silver.**—When pure solutions of silver salts are carefully reduced, silver is produced as fine particles too small to settle, and forms strongly-coloured *colloidal solutions.*

A colloidal silver may be prepared by adding to 2 c.c. of 0·01N silver nitrate solution, 4 c.c. of a solution of 0·01N crystallised sodium citrate solution and 1 c.c. of 0·001M hydroquinone solution—stirring well. The solutions must all be strictly neutral except the sodium citrate, which should be just alkaline (1–3 drops $NH_4OH$ per 100 c.c. of neutral solution may be added). The successful preparation of these colloidal solutions requires scrupulous cleanliness of apparatus and purity of materials.

Colloidal silver preserved from precipitation with albumen, etc., is used in medicine as a disinfectant of a non-irritating character, suitable for ophthalmic cases, etc

**305. Oxides of Silver.**—Silver forms two oxides, both unstable,

Silver oxide $Ag_2O$,
Silver peroxide $Ag_2O_2$.

**306. Silver Oxide $Ag_2O$.**—Silver hydroxide does not appear to exist, and silver oxide is formed directly when caustic potash is added to silver nitrate solution,

$$2KOH + 2AgNO_3 = Ag_2O + H_2O + 2KNO_3.$$

It is filtered off, washed and dried below 100° C.

Silver oxide is a black powder. It is not quite insoluble in water (1 : 15,360), and the solution formed is alkaline.

When heated, silver oxide loses its oxygen at about 300° C.,

$$2Ag_2O = 4Ag + O_2.$$

Silver oxide is soluble in ammonia, for the same reason as silver chloride (*q.v.*). Silver oxide is sometimes used to replace a halogen group in a compound by hydroxyl, particularly in organic chemistry. Thus, if tetramethylammonium chloride be treated with silver oxide the free base is produced,

$$2N(CH_3)_4 . Cl + Ag_2O + H_2O = 2N(CH_3)_4 . OH + 2AgCl.$$

**307. Silver Peroxide $Ag_2O_2$** is probably not a true peroxide. It may be made by mixing 1,000 c.c. 3 per cent. $K_2S_2O_8$ with 100 c.c. 10 per cent. silver nitrate, and allowing the precipitate to settle out. It is washed by decantation and dried at room temperature. It is a black powder decomposed by acids, forming silver salts and oxygen. It is a very powerful oxidising agent, oxidising ammonium salts to nitrates, etc.

**308. Reactions characteristic of Silver Ion.**—Silver salts give, with chlorides, bromides and iodides, characteristic precipitates of the silver halides (*q.v.*).

$$AgNO_3 + KCl = AgCl \downarrow + KNO_3$$

or
$$Ag^+ + Cl^- \rightleftharpoons AgCl \downarrow .$$

These precipitates are not soluble in dilute nitric acid.

Silver salts give precipitates with the salts of a vast number of other acids, the only common salts which do not give precipitates being the nitrates, chlorates, perchlorates, fluorides, sulphates, and permanganates.

*White precipitates of the silver salt are given by*
- Sulphate (in strong solution).
- Chloride.
- Cyanide.
- Thiocyanate.
- Ferrocyanide.
- Pyrophosphate.
- Metaphosphate.
- Borate.
- Sulphite.
- Thiosulphate.
- Oxalate.
- and many organic acids.

*Pale yellow precipitate by*
- Bromides.

*Yellow precipitates by*
- Iodide.
- Phosphate.
- Arsenite.

*Orange precipitate by*
- Ferricyanide.

*Chocolate-brown precipitate by*
- Arsenate.

*Red precipitate by*
- Chromate.

*Black precipitates by*
- Sulphide.
- Hydroxide.
- and some reducing agents.

The type of precipitate given by silver nitrate and a soluble salt affords us, then, a good idea of its nature, especially as the precipitates are to be distinguished by solubility in various reagents as well as by colour.

Solutions of silver salts are decomposed by all other metals, except gold and the platinum metals, yielding metallic silver and a salt of the metal,

$$2AgNO_3 + Cu = Cu(NO_3)_2 + 2Ag.$$

or
$$2Ag^+ + Cu = Cu^{++} + 2Ag.$$

Silver ion is reduced to metallic silver by most reducing agents, including organic matter in light, free hydrogen (with difficulty), arsine, stibine, hypophosphites, phosphites, ferrous salts, dextrose, and many organic reducing agents.

**309. Electroplating.** — Silver salts, like others, are readily decomposed by electrolysis. Objects are coated with silver— *electroplated* — by making them the cathode of a cell, of which the anode is a silver plate and the liquid a solution of a silver salt. To obtain a coherent deposit which will not flake off, the objects must be very clean, and the liquid must contain a very low concentration

of silver ion. This latter condition is ensured by using as electrolyte a solution of potassium argentocyanide. The argentocyanide ion is in equilibrium with only a very small

$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$$

concentration of silver ion. During electrolysis the silver ions, $Ag^+$, are discharged at the cathode and are deposited on the objects to be plated, while the cyanide ions discharge at the anode with which they immediately combine, re-forming silver cyanide. This dissolves to form the argentoyanide ion, and thus the bath remains unaltered in composition, the silver being simply transferred from anode to cathode.

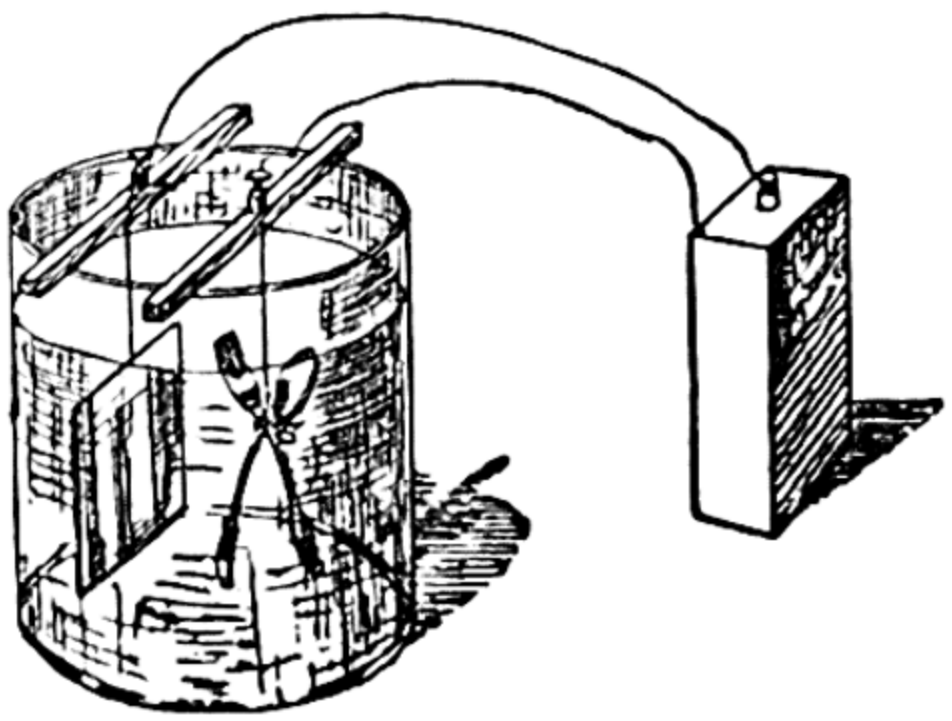

FIG. 83.—Electroplating.

SALTS OF SILVER

**310. Silver Carbonate $Ag_2CO_3$** is made by the usual methods. It decomposes when gently heated, giving free silver,

$$2Ag_2CO_3 = 4Ag + 2CO_2 + O_2.$$

**311. Silver Nitrate $AgNO_3$.**—Silver nitrate is the most important salt of silver. It is prepared by dissolving silver in nitric acid and crystallising the solution produced. It is purified by recrystallisation.

Silver nitrate crystallises without water of crystallisation in colourless rhombic tabular crystals. It melts at 212° C.

Silver nitrate is exceedingly soluble in water. At 0° C. 100 gms. of water dissolve 121·9 gms. of the salt and at higher temperatures all mixtures of the salt and water up to pure melted silver nitrate can exist. Thus at 133° C. we may equally well say that 100 gms. of water dissolve 1,941 gms. of silver nitrate or that 100 gms. of melted silver nitrate dissolve 5·15 gms. of water.

Silver nitrate decomposes when heated, giving silver nitrite at lower temperatures, but at a red heat giving silver, oxides of nitrogen, nitrogen and oxygen. The main reaction is

$$2AgNO_3 = 2Ag + 2NO_2 + O_2.$$

Silver nitrate readily oxidises organic matter, being reduced to black finely-divided metallic silver, especially under the action of light.

This leads to its use as a caustic, *lunar caustic*, in medicine. Warts, etc., when rubbed with it are killed and gradually disappear.

The use of silver nitrate as a marking ink and as a hair dye is dependent on this action.

Silver nitrate has also a number of other reactions, which are characteristic of the silver ion, $Ag^+$.

*Silver sulphate* $Ag_2SO_4$ is sparingly soluble in water (1 : 200 in the cold). It forms alums, such as

$$Ag_2SO_4 . Al_2(SO_4)_3 . 24H_2O$$

*Silver sulphide* $Ag_2S$ is a black substance made by precipitating a silver salt with hydrogen sulphide, or by the action of sulphur on silver. It is insoluble in dilute acids.

**312. Halides of Silver.**—*Silver fluoride* AgF differs from the other halides by being soluble in water.

*Silver chloride* AgCl is found native as *horn-silver*, so called from its translucent appearance. It is usually prepared by the action of hydrochloric acid on silver nitrate,

$$AgNO_3 + HCl = AgCl + HNO_3,$$

or

$$Ag^+ + Cl^- = [Ag]\,[Cl].$$

It may also be made by the passing of chlorine over heated silver,

$$2Ag + Cl_2 = 2AgCl.$$

Silver chloride forms a white curdy or flaky precipitate or a white powdery solid, which turns blue in the light (*v.* § 315). It fuses at 460° C. and solidifies to a horny translucent mass. Silver chloride is nearly insoluble in water, about 1·6 milligrams dissolving in a litre of water. Silver chloride dissolves in ammonia solution, potassium cyanide solution and sodium thiosulphate solution, in each case forming complex ions.

The theory of the solution of an 'insoluble' salt in another solution which forms a complex ion with one of its salts is discussed in § 120. In the cases of cyanide and of ammonia, silver ion readily forms a complex cyanide ion $Ag(CN)_2^-$, and also a complex ion, $Ag(NH_3)_2^+$, both of which are in equilibrium with very minute concentrations of silver ion. The concentrations of silver ion, which can be in equilibrium with ammonia or cyanide ion are so small that they will not, as a rule, reach the solubility product of even so 'insoluble' a salt as silver chloride, and consequently this will dissolve.

A less accurate way of regarding the matter is to look on the process as the formation of double salts, silver ammonia chloride, sodium argentocyanide and silver sodium thiosulphate. These salts are certainly formed and can be isolated,

$$AgCl + 2NH_3 = Ag(NH_3)_2Cl$$
$$AgCl + 2KCN = KAg(CN)_2 + KCl.$$

Silver chloride is, on the whole, a very unreactive substance.



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Thus it is almost unaffected by treatment with acids. Silver chloride may be converted into silver by fusing it with sodium or potassium carbonate, or, better, cyanide,

$$2Na_2CO_3 + 4AgCl = 4NaCl + 4Ag + 2CO_2 + O_2.$$

It may also be reduced by heating it in a current of hydrogen,

$$2AgCl + H_2 = 2Ag + 2HCl,$$

or by leaving it in contact with zinc under dilute acid.

$$2AgCl + Zn = ZnCl_2 + 2Ag.$$

Silver chloride is converted into silver bromide or iodide when left in contact with potassium bromide or iodide for some time. The solubility product of silver chloride is $1{\cdot}2 \times 10^{-10}$, and therefore

$$[Ag^+]\,[Cl^-] = 1{\cdot}2 \times 10^{-10}$$

and

$$[Ag^+] = 1{\cdot}1 \times 10^{-5}$$

in a saturated solution. But the solubility product of silver iodide is only $1{\cdot}7 \times 10^{-16}$ and so a saturated solution is formed when

$$[Ag^+]\,[I^-] = 1{\cdot}7 \times 10^{-16}$$

In a normal solution of potassium iodide $[I^-] = 1$, and so silver iodide will deposit until $[Ag^+]$ is only $1{\cdot}7 \times 10^{-16}$. This is much less than the concentration of silver ion provided by the dissociation of the chloride and accordingly the silver ion formed by the solution of silver chloride is converted into solid silver iodide and more silver chloride dissolves, forming more silver ion, which is again precipitated. This process continues till only a trace of silver chloride remains unconverted into the iodide.

Silver chloride and most other silver salts absorb ammonia gas, forming compounds such as $2AgCl \,.\, 3NH_3$, etc.

**313. Silver Bromide AgBr** much resembles the chloride and is made by corresponding methods. The bromide is pale yellow and is not turned blue in light, though it is otherwise affected (§ 316). It also differs from the chloride in being less soluble in water and less soluble in ammonia.

**314. Silver Iodide AgI** resembles the bromide. It is primrose-yellow in colour. It is very insoluble in water and practically insoluble in ammonia. It is remarkable in that it contracts when heated and expands when cooled over the range $-40°$ C. to $147°$ C.

**315. Action of Light on Silver Salts. Photography.**—The effect of light on silver salts was noticed by Davy; fixation of the image by hypo-sulphites was discovered by Herschel in 1839, and the camera was used at quite an early date (1841) by Fox Talbot.

**316. The photographic plate** consists of glass coated with a suspension of silver bromide (with a little silver iodide) in gelatine. The size of grains of silver halide determines the sensitiveness of the plate. When this is exposed for a short time to light, as for example, in a camera, no visible effect is produced. None the less, a *latent image* is formed on the plate and the parts which

have become exposed to light can now be *developed*, *i.e.*, reduced to silver by the action of a suitable reducing agent. The latent image consists of minute particles of silver,[1] too scanty in quantity to be visible. One atom of silver is formed by each quantum of light. These particles of silver occupy only a part of the grain of silver bromide, and development reduces to silver the whole of those grains in which any silver has already been produced by the light.

**317. Development.**—All developers are fairly powerful reducing agents The simplest, perhaps, is ferrous oxalate; most of those in general use are aminophenols. Their chemical action on the grains of silver bromide is, in general,

$$AgBr + HX = Ag + HBr + X.$$

The silver of the latent image evidently acts catalytically on the silver bromide of the grains in which it is contained, causing them to be reduced. The mechanism of the reaction is not understood.

**318. Fixation.**—The developed image consists of metallic silver and silver bromide. From this the silver bromide must be removed. Any solvent for silver bromide which does not affect silver may be used and the usual one employed is sodium thiosulphate (hypo.). Silver sodium thiosulphate is formed,

$$2AgBr + 3Na_2S_2O_3 = Na_4[Ag_2(S_2O_3)_3] + 2NaBr,$$

or

$$AgBr \rightleftharpoons Ag^+ + Br^-$$

$$2Ag^+ + 3[S_2O_3]^{--} \rightleftharpoons [Ag_2(S_2O_3)_3]^{----}.$$

Potassium cyanide solution can also be employed. The plate is washed thoroughly, for the thiosulphate has a solvent effect on silver, and then dried.

**319. Printing and Toning.**—The chemistry of printing and fixing a bromide paper is similar to that described for a plate. Printing-out paper has a basis of silver chloride. The action is continued till a considerable amount of silver is produced. Fixation leaves this image of a disagreeable red tone. It is therefore immersed, before fixation, in a weak solution of gold chloride $AuCl_3$ (or sodium chloraurate $NaAuCl_4 . 2H_2O$).

The reaction is $3Ag + AuCl_3 = 3AgCl + Au$. The grains of silver are thus coated with a fine layer of gold. Fixing and toning are ordinarily carried on simultaneously. In self-toning papers the gold salt is incorporated in the emulsion

Numerous other processes of photographic printing are based on various reactions brought about by light, *e.g.*, reduction of organic ferric salts, decomposition of diazonium compounds, action of dichromates on gelatin, etc.

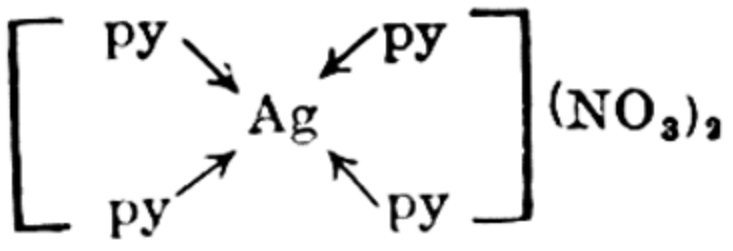
**320. Silver Residues.**—Solutions and precipitates containing silver are collected in most laboratories in a 'silver residues' bottle. The silver is best recovered by precipitating it as the chloride by addition of hydrochloric acid. If the residues contain cyanides, as is often the case, the precipitating and filtration should be performed in a good fume cupboard or the open air, as the extremely dangerous vapour of hydrogen cyanide may be evolved. The precipitate of silver chloride is filtered off, washed and warmed with caustic soda solution and glucose. When reduced to metallic silver, the precipitite

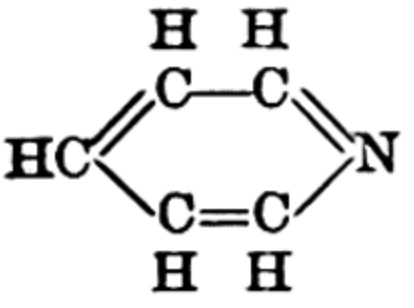
[1] The theory of the production of a reducible sub-halide (*e.g.*, $Ag_2Cl$) is improbable in view of the work of Hartung.

is washed, dried and mixed with some twice its weight of sodium carbonate and fused in a clay crucible.[1]

**320a. Bivalent Silver.**—Silver, as being analogous to copper, might be expected to form bivalent compounds. These have been discovered, but are only stable in the form of complex compounds with such bases as pyridine.

A typical example is tetrapyridinoargentic nitrate




where py = 

It is made by electrolysing an aqueous solution of silver nitrate and pyridine, isolating the anode by means of a porous pot. Nitrate ions are discharged at the anode and react thus,

$$AgNO_3 + NO_3 + 4py = [Ag(py)_4]\,(NO_3)_2.$$

The bivalent silver compounds are orange in colour They would naturally be coloured, for the loss of *two* electrons makes the 4-quantum group incomplete.

They are most powerful oxidising agents, converting manganous salts to permanganates.

**320b. Argentic fluoride $AgF_2$** has been prepared by the action of fluorine on silver halides. It is a powerful fluorinating agent.

**321. Detection and Estimation.**—Silver is readily detected by the formation of its insoluble chloride, AgCl, when a solution containing silver is treated with hydrochloric acid,

$$Ag^+ + Cl^- \rightleftharpoons AgCl\downarrow .$$

Lead salts and mercurous salts give similar insoluble chlorides. If these metals may also be present in the material tested, lead chloride is removed from the precipitate by treating it with boiling water, in which it is soluble. The residue may contain silver chloride and mercurous chloride. The former may be dissolved out by means of ammonia (§ 312) and reprecipitated with nitric acid. The precipitate of silver chloride is flocculent and white, becoming blue on exposure to light.

Silver is estimated by precipitation as above, the precipitate being filtered off, dried at 110° C. or above and weighed. It may also be estimated volumetrically by titration with standard sodium chloride. A standard solution of the latter salt is run from a burette into the solution of the silver salt contained in a stoppered bottle. After each addition of the chloride the solution is shaken so that the silver chloride shall settle out, leaving a clear liquid. The end-point is shown by a drop of the sodium chloride solution giving no

[1] A Bunsen burner will not produce a high enough temperature The crucible is best placed on a bright glowing coal fire.

cloud of silver chloride as it enters this supernatant liquid. The calculation is based on the equation,

$$AgX + NaCl = AgCl + NaX,$$

one atom of silver corresponding to one molecule of sodium chloride.

Potassium chromate is sometimes used as an indicator in the above titration. The silver solution is neutralised and is run from the burette into standard sodium chloride to which a little of the chromate solution has been added. While any chloride remains the reaction,

$$Ag^+ + Cl^- \rightleftharpoons AgCl \downarrow,$$

results in the precipitation of the very insoluble silver chloride only. As soon as the chloride has disappeared (or been reduced to a very minute concentration), the chromate ion reacts, forming red silver chromate,

$$2Ag^+ + CrO_4^{--} \rightleftharpoons Ag_2CrO_4.$$

The appearance of this red colour marks the end of the reaction.

Silver is also titrated by the Volhard method, which depends on the formation of the insoluble silver thiocyanate AgCNS. A standard solution of ammonium thiocyanate is run into the solution of a silver salt (which must not be strongly acid) to which a little iron alum solution has been added. The end-point is marked by the appearance of a red colour due to ferric thiocyanate (§ 1166),

$$NH_4CNS + AgNO_3 = AgCNS + NH_4NO_3.$$

Adsorption indicators are now much used. Certain dyes (*e.g.*, dichlorofluorescein) are added to the solution of chloride to be titrated. The silver nitrate is run in. The silver chloride formed adsorbs chloride ion as long as any remains.

At the end-point, when a minute excess of silver nitrate is present, this adsorbed chloride is removed, and in place of it the silver chloride adsorbs the ions of the dye. The effect of this is that the suspension of white silver chloride in the pale yellow dye solution becomes strongly pink, marking the end-point clearly. Weak acids, but not mineral acids, may be present.

## GOLD Au, 197·2

**322. Historical.**—Gold is the most anciently known of metals. The Egyptians worked gold from the earliest time and gave it the significance, first of all, of Hathor, the cow-goddess of fertility, and later, of Ra the sun-god. It has universally been the precious metal *par excellence*, for indeed it is unrivalled in its colour and lustre, its imperishability and its ductility which has enabled it to be worked into so many objects of beauty. Though to-day it has lost the position of being the chief medium of currency it still represents the final reserve of wealth and lies in thousands of tons in the coffers of the great banks.

**323. Occurrence.**—The only source of gold of any importance is the native metal. This is found widely distributed in minute traces. The chief minerals that contain it in workable quantities are certain 'reefs' of quartz and certain alluvial gravels.

The chief quartz deposits are in South Africa, and auriferous gravel is found chiefly in the western parts of North America. Quartz containing as little as ·001 per cent. of gold and gravels containing as little as ·00003 per cent. can be profitably worked.

**324. Extraction of Gold.**—Auriferous gravels are worked by washing them with water. Streams of water are projected on to the deposit and the water as it runs off carries the gold dust together with much sand, clay, etc., in suspension. The water is then directed through long wooden troughs, where the gold dust is first deposited owing to its high specific gravity, and is caught by battens nailed across the bottoms of wooden troughs. The clay, etc., being lighter, is carried away.

Gold-bearing quartz is usually treated by the cyanide process. Gold reacts slowly with sodium cyanide, forming sodium auro-cyanide.

The reactions are probably :—

(1) $2H_2O+2Au+4NaCN+O_2=2NaAu(CN)_2+2NaOH+H_2O_2$.

(2) $H_2O_2+4NaCN+2Au=2NaAu(CN)_2+2NaOH$.

The nature of these reactions is still in dispute.

The ore is crushed very finely by stamp-mills and placed in large vats with false bottoms. Very weak sodium cyanide solution, 0·15 per cent. or less, is allowed to percolate through it. The cyanide solution then runs through long boxes filled with zinc shavings. The gold is precipitated as a black slime,

$$2NaAu(CN)_2 + Zn = 2Au + Na_2Zn(CN)_4,$$

which is then melted with some oxidising agent to remove the zinc.

**325. Refining of Gold.**—Crude gold commonly contains silver and copper. It is usually purified by 'parting' with sulphuric acid. If the alloy contains more than 30 per cent. of gold, the proportion is reduced by melting it and alloying it with silver ; the object of this process is to make the gold alloy readily attacked by the acid.

The alloy is granulated by pouring it into water and then boiled with concentrated sulphuric acid in cast-iron pots.

The silver and copper react with the acid and the gold remains. The gold is then melted and cast into ingots. The acid liquor is diluted and treated with scrap copper, when the silver is precipitated,

$$Ag_2SO_4 + Cu = CuSO_4 + 2Ag.$$

*An electrolytic method* is sometimes used, similar to that described under copper (p. 297). The anode is a slab of the impure alloy, the cathode a sheet of silver, and the electrolyte silver nitrate with some nitric acid. The silver deposits on the cathode and dissolves (with any copper) from the anode. The gold remains at the anode.

The anodes may then be cast into slabs and again electrolysed with a gold cathode and a hydrochloric acid and gold chloride electrolyte. Pure gold deposits on the cathode while the silver remains as a residue of chloride.

**326. Properties of Gold.**—Gold is a metal of familiar yellow tint. Very thin leaves of gold transmit a green light. Gold is soft, though harder than lead, and is extremely malleable and ductile. Gold leaf is produced simply by hammering strips of gold interleaved at first with vellum, and when thinner with gold-beaters' skin, made from the cæcum of the ox; the metal can be beaten out to a thickness of ·00008 mm. A cube of gold, of edge 3 inches in length, could be beaten out to cover an acre. Gold melts at 1,064° C. Its density is very high, 19·3, only exceeded by rhenium, platinum, iridium and osmium.

Gold is unaffected by oxygen or by any of the constituents of the air. It is unattacked by any of the acids (except iodic acid and selenic acid), nor is it attacked by alkalis.

Gold is attacked by the halogens and therefore by *aqua regia*, which evolves chlorine (p. 697) and converts gold into chlorauric acid,

$$2Au + 3Cl_2 + 2HCl = 2HAuCl_4.$$

Gold is slowly dissolved by potassium cyanide solution as described in § 324 above, also by aqueous solutions of sulphides and thiosulphates.

**327. Colloidal Gold.**—Gold, being quite unattacked by water, can persist as a colloidal solution for long periods. Such colloidal solutions are prepared by Bredig's method (*v.* § 92 (2) ) or by reduction of very pure dilute solutions of gold chloride. The following method may be used:

Make up a solution of 0·1 gm. of 'gold chloride' (chlorauric acid) in 30 c.c. of distilled water. Add this to 400 c.c. of boiling distilled water. Add to this 2 c.c. of a 0·05 molar solution of Rochelle salt, drop by drop. Blue colloidal gold is first formed and gradually becomes red. To ensure success very pure distilled water, twice re-distilled through a tin condenser, should be used. All vessels must be of resistance glass, previously well steamed to remove alkali (§ 201).

These colloidal solutions have various colours: red, blue, violet and green, depending upon the size of the particles. Examined by the ultramicroscope —a powerful microscope arranged to give a brilliant illumination, so directed as not to pass into the lens of the microscope, but rather to light up any minute particles brilliantly against a dark background—these solutions are seen to be filled with minute particles discernible as brilliant specks in vigorous

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and chaotic motion. The gold is evidently in minute granules so small as to be held suspended in perpetual vigorous motion by the buffets of the vibrating molecules of the liquid. These solutions are readily precipitated in presence of charged ions and are therefore difficult to preserve unless the materials used are very pure.

When gold is precipitated together with another colloid it may form a solid colloidal solution of fine purple tint—the so-called *purple of Cassius*. This pigment is made by mixing a solution of stannous chloride containing stannic chloride with a dilute solution of gold chloride. Probably metallic gold and colloidal stannic acid are formed together :

$$2AuCl_3 + 3SnCl_2 = 2Au + 3SnCl_4$$
$$SnCl_4 + 4H_2O \rightleftharpoons Sn(OH)_4 + 4HCl.$$

The colloidal stannic acid 'protects' the gold particles and the colour of the colloid is permanently preserved. Aluminium may be substituted for tin if an alkaline solution of glucose is used as reducing agent.

**328. Atomic Weight of Gold.**—A value near 200 is indicated by Dulong and Petit's law, the Periodic law, and the molecular weight of gold compounds in solution. The equivalent of gold and its exact atomic weight have been determined :

(1) By converting a known weight of auric chloride $AuCl_3$ into silver chloride 3AgCl.

(2) By the electrochemical method (§ 280).

(3) By heating potassium bromoaurate $KAuBr_4$ and weighing the residual gold.

The best representative value is 197·21.

**329. Oxides of Gold.**—Two oxides exist :

| | |
|---|---|
| Aurous oxide | $Au_2O$. |
| Auric oxide | $Au_2O_3$. |

These oxides of gold are made by precipitating aurous and auric chlorides respectively with caustic potash, washing and drying the precipitate.

Both oxides are very unstable, and on gentle heating yield metallic gold and oxygen.

**330. Gold Salts.**—All the gold salts are decidedly unstable.

*Auric sulphate* $Au_2(SO_4)_3$ is very unstable, depositing gold on warming.

*Auric nitrate* $Au(NO_3)_3$ is only stable in presence of concentrated nitric acid.

*Aurous nitrate* $AuNO_3$ has been prepared.

*Aurous chloride* AuCl is made by heating auric chloride to 170° 180° C. It is insoluble in water (cf. cuprous and silver chlorides). It is decomposed by water to auric chloride and metallic gold.

**331. Auric Chloride, Gold Trichloride $AuCl_3$.**—When gold is dissolved in *aqua regia* and the solution concentrated yellow crystals separate. These are hydrated chlorauric acid $HAuCl_4 . 4H_2O$. This is the substance sold as "gold chloride." When this is heated in a current of chlorine at 200° C auric chloride $AuCl_3$ is formed as red crystals.

Auric chloride is readily decomposed in neutral solution to aurous chloride and hydrogen peroxide,

$$AuCl_3 + 2H_2O = AuCl + 2HCl + H_2O_2.$$

On heating it forms, at first, aurous chloride, and finally gold and chlorine,

$$AuCl_3 = AuCl + Cl_2$$
$$2AuCl = 2Au + Cl_2.$$

Reducing agents readily reduce it to metallic gold.

With hydrochloric acid it forms chlorauric acid $HAuCl_4 . 4H_2O$. The chloraurates of sodium and potassium are used for toning prints in photography (*v.* § 319). Chlorauric acid is a more stable compound than auric chloride.

**332. Detection of Gold.**—One of the most sensitive tests for the detection of gold salts is the addition of a mixture of dilute stannous and stannic chlorides to the solution suspected of containing it. A purplish precipitate, the so-called 'purple of Cassius,' consisting of a mixture of hydrated stannic oxide and finely-divided gold, is produced at once on heating, but only very slowly in the cold.

**333. Estimation of Gold.**—Gold is usually estimated by assaying. The gold ore is very finely crushed and a weighed amount of it is mixed with lead oxide, charcoal, borax and soda. It is then fused in a crucible and a button of metallic lead alloyed with any gold and silver present settles to the bottom. This lead button is heated on a small cupel (p. 310) of magnesia or bone ash in a muffle furnace, until all the lead has changed to oxide. This melts and soaks into the cupel and leaves behind a bead of gold and silver. This bead is flattened and heated with nitric acid, which dissolves out the silver. It is then heated to redness to make its particles cohere, and weighed on a delicate assay balance.

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# CHAPTER XII

## THE ALKALINE EARTH METALS

**334. Introductory.**—Group II. of the periodic table consists of the elements,

| II. A. | II. B. |
|---|---|
| Beryllium. | |
| Magnesium. | |
| Calcium. | |
| | Zinc. |
| Strontium. | |
| | Cadmium. |
| Barium. | |
| | Mercury. |
| Radium. | |

Group II. A has an electronic structure, comprising one or more complete electron layers, together with two outer valency electrons. Thus the calcium atom has the structure 2.8.8.2 and the radium atom 2.8.18.32.18.8.2. The elements of this group are therefore bivalent. The elements of Group II. B have also two outer valency electrons, and are bivalent. They, however, have not a completed set of inner electrons, but unlike the incomplete groupings of the transition elements, its inner group of 18 is too stable to be able to furnish any valency electrons. Thus the zinc atom has the structure 2.8.18.2, and the mercury atom 2.8.18.32.18.2. This group then does not resemble the transition elements, the 'cores' of which can furnish valency electrons. Their salts are colourless and they are of fixed electrovalency (but see § 440).

The elements of Group II. A, the alkaline-earth metals, are bivalent, and are characterised by a *strong electropositive character*, being second only to the alkali metals in this respect. Connected with this fact, as we see in § 126, are the properties which follow.

The elements are highly reactive. They burn in air, readily decompose water and react easily with acids. Their oxides are strongly basic and their hydroxides are alkaline in character. Their salts are stable.

The metals of the alkaline earths differ from the alkali metals in that they are somewhat less reactive. Moreover, a great difference in the practical methods of preparing and manipulating their compounds is occasioned by the fact that, while the salts of the alkali metals are almost all freely soluble, many of the salts of the alkaline earth metals are insoluble in water. This circumstance

renders the behaviour of such a salt as sodium carbonate entirely different from that of calcium or magnesium carbonate.

## BERYLLIUM Be, 9·013

**335. Sources.**—Beryllium, also known as *glucinum*, is contained in the minerals, beryl and emerald.

Beryl is a not uncommon mineral and is the source of beryllium compounds, which are prepared from it as follows :—

Beryl, which is beryllium alumino-silicate $3BeO \cdot Al_2O_3 \cdot 6SiO_2$ may be finely powdered and fused with sodium silicofluoride. The product contains silica, and also sodium, aluminium, and beryllium as fluorides, which are extracted by boiling water. The addition of a slight excess of caustic soda precipitates beryllium hydroxide, together with a little aluminium hydroxide. The precipitate is filtered off and dissolved in sulphuric acid, and from this solution beryllium sulphate may be crystallised.

Metallic beryllium is prepared by the electrolysis of fused sodium beryllium fluoride or by the action of magnesium on beryllium fluoride.

**336. Atomic weight of Beryllium.**—That beryllium has an approximate atomic weight of 9 was established with some difficulty. The equivalent is about 4·5. Dulong and Petit's law breaks down here, giving at ordinary temperatures a value for the atomic weight of about 15, but at higher temperatures a value approximating to 9. Its likeness to magnesium, etc., is not so great as to necessitate its being placed in Group II., for it shows quite as great an analogy to aluminium. The question was settled by a study of the vapour density of the chloride. The value for the molecular weight of $BeCl_2$ would be

| | | |
|---|---|---|
| | Be . . . . | $2 \times 4{\cdot}5$ |
| | $Cl_2$ . . . . | 71 |
| | | 80 |
| and for $BeCl_3$ | Be . . . . | $3 \times 4{\cdot}5$ |
| | $Cl_3$ . . . . | 106·5 |
| | | 120 |

The actual results showed a vapour density near 40, giving a molecular weight not far from 80, agreeing with the former value.

The specific gravity of its solutions showed analogies to the elements of Group II. rather than Group III., and so favoured the view that it was bivalent ; as did also the impossibility of accommodating an element of atomic weight, 13·5, in Group III. of the Periodic table. It was concluded then that the atomic weight was about 9 and the most recent and exact determinations show a value of 9·02.

**337. Properties of Beryllium and its Compounds.**—Beryllium is a hard white metal. Its melting point is high (*c.* 1,400° C.) and its density is very low, 1·93. Its chemical properties are, on the whole, similar to those of magnesium (*q.v.*), but it does not decompose water even at a red heat, an impervious layer of oxide probably being formed. It reacts with caustic alkalis in the same manner as

zinc or aluminium. It seems probable that beryllium alloys will find considerable uses in the future, for they are light, strong and not readily subject to corrosion. Beryllium is the most effective hardening agent for copper.

*Beryllium oxide* BeO is a white powder, insoluble in water. It forms beryllium salts with acids, and like zinc forms salts with alkalis such as $Be(OK)_2$.

Beryllium forms a series of salts in which the metal is divalent. These resemble, on the whole, the salts of magnesium. Its behaviour, however, differs in some respects from that of the other members of Group II. A, and resembles that of aluminium (cf. resemblance of lithium to magnesium, § 220). In the first place, its oxide and hydroxide have both basic and also feebly acidic characteristics. In the second place its halides such as beryllium chloride are easily hydrolysed by water,

$$BeCl_2 + 2H_2O \rightleftharpoons Be(OH)_2 + 2HCl.$$

Thirdly, it forms a series of basic salts with great ease, one of which, the basic acetate, is remarkable in that it is volatile at comparatively low temperatures. The peculiar behaviour of beryllium is due to the small size of its atom. This causes it to form complex compounds with great ease, and to be ionised to a less extent than the other elements of the group.

## MAGNESIUM Mg, 24·32

**338. History and Occurrence.**—Magnesium compounds, such as the sulphate and carbonate, have been known since early times. The word magnesia dates back to classical times, but it is not at all certain that any of the compounds to which it was applied contained magnesium. The metal magnesium was first prepared by Davy, in 1808, by electrolysing the chloride.

Magnesium occurs chiefly as *magnesite*, $MgCO_3$ and *dolomite*, ($MgCO_3 + CaCO_3$), the latter mineral forming whole mountain ranges. It is also found as *kieserite*, monohydrated magnesium sulphate, and together with potassium salts in *kainite* and *carnallite* (§ 255). Many minerals are double silicates of magnesium and some other metal. Among these are talc, meerschaum, asbestos, and serpentine.

Magnesium sulphate is contained in many mineral springs and magnesium chloride is found in sea water, from which it is extracted at Freeport, in Texas, and used in the preparation of the metal.

**339. Preparation of Magnesium.**—Magnesium is made by the electrolysis of the fused chloride,

$$MgCl_2 = Mg + Cl_2.$$

Magnesium is prepared industrially by electrolysis of a mixture of fused magnesium chloride, sodium chloride and potassium chloride, the latter salt preventing the decomposition of the chloride by

hydrolysis (§ 345). One type of cell used is that shown in Fig. 84. The fused chlorides are kept hot by a furnace (not shown). The cathode is the iron cell itself, the anode a carbon rod enclosed in a porcelain casing, through which the chlorine produced passes away. The magnesium collects at the top of the cell. Care must be taken to avoid oxidation, as this prevents the globules of metal forming a coherent mass. A current of a reducing gas is therefore led through the cell and a reducing agent, such as carbon, is sometimes added.

A more recent process utilises the equilibrium set up between magnesia, carbon, magnesium, and carbon monoxide, at high temperatures.

$$MgO + C \rightleftharpoons Mg + CO$$

Finely divided magnesia and coke, made up into pellets, is fed into an electric furnace, operating between 1950–2050° C., at which temperatures the equilibrium is well to the right. The gaseous magnesium and carbon monoxide issuing from the furnace is rapidly cooled in a stream of natural gas to freeze the equilibrium, and the finely-divided magnesium so produced is retained in filter bags, later to be refined by distillation.

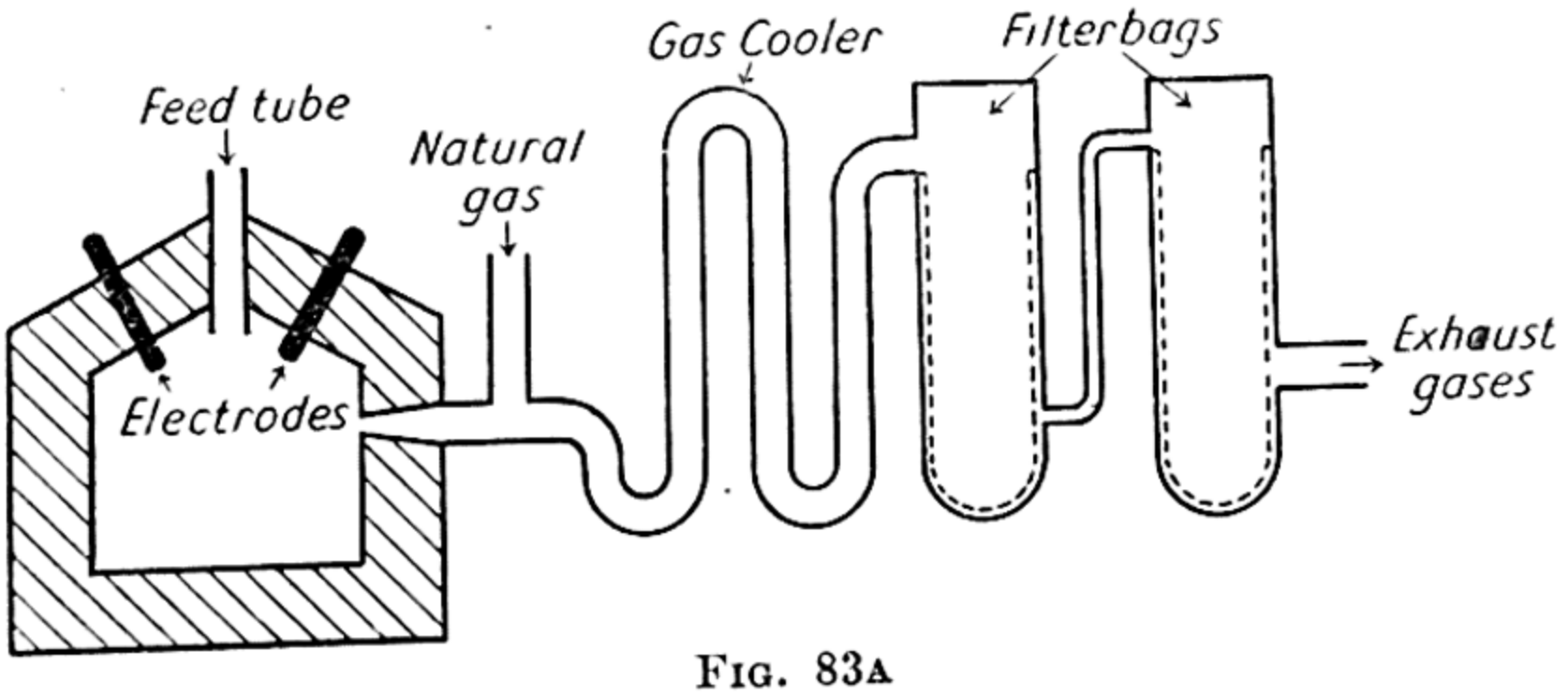


FIG. 83A

**340. Properties of Magnesium.**—Magnesium is a silver-white metal. It melts at 650± 2° C. and boils at about 1,100° C. Magnesium has a density of 1·75. It is strong and can be worked. Its lightness would bring it into use for aeroplane parts, etc., were it not that it soon corrodes in contact with moisture.

Its alloy with aluminium, *magnalium*, has found considerable use where a very light and strong metal is required.

Magnesium is not affected by dry air at ordinary temperatures, but when heated, burns with an exceedingly brilliant white flame. Many applications of this in photography and pyrotechny have been made. Flash-powder for photographic use may be made from magnesium and an oxidising agent such as potassium permanganate.

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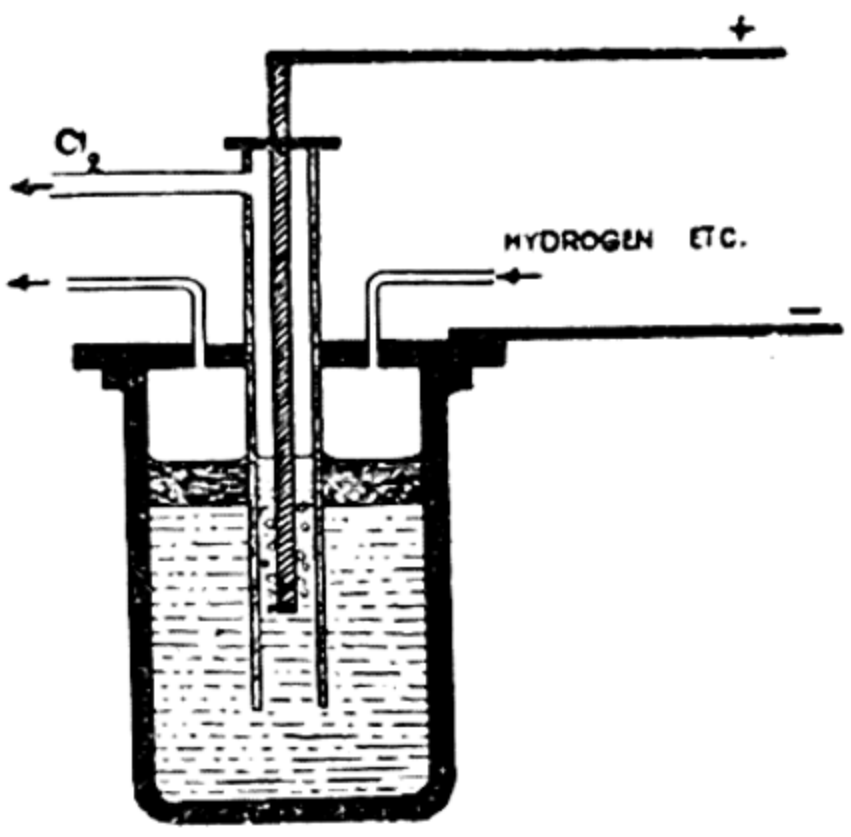


FIG. 84.—Preparation of magnesium by electrolysis.

Magnesium reacts readily with most of the non-metals, such as oxygen, the halogens, sulphur, phosphorus, arsenic and nitrogen, burning brilliantly in chlorine and the vapours of bromine, iodine and sulphur. The nitride (*q.v.*) is very readily formed. Magnesium reacts with water, slowly in the cold and rapidly when boiling, forming magnesium hydroxide and hydrogen,

$$Mg + 2H_2O = Mg(OH)_2 + H_2.$$

It burns when heated in steam, forming the oxide and hydrogen,

$$Mg + H_2O = MgO + H_2.$$

With dilute acids, hydrogen and a salt are formed. Magnesium is the only metal which gives hydrogen with dilute nitric acid.

Alkalis do not attack magnesium. Magnesium being very electro-positive in character readily displaces nearly all of the metals from their salts, *e.g.*,

$$Mg + Pb(NO_3)_2 = Mg(NO_3)_2 + Pb$$

or

$$Mg + Pb^{++} = Mg^{++} + Pb.$$

Magnesium decomposes most oxides. Thus, when heated in carbon dioxide it burns, forming magnesium oxide and depositing carbon,

$$2Mg + CO_2 = 2MgO + C.$$

*Uses.*—The chief uses of magnesium are in photographic flash-lights and flares to be used for signalling, or as fireworks. In chemical work it finds a use as a reducing agent, and in the preparation of the Grignard reagent, much used in organic chemistry.

**341. Atomic Weight of Magnesium.**—The approximate value of 24 for the atomic weight is indicated by Dulong and Petit's law, and the Periodic table and the molecular weights of its salts in solution. The equivalent is 12·15 and the element is therefore bivalent.

The best atomic weight determinations depend on the change of weight when magnesium chloride is converted into silver chloride, and when magnesium sulphate is converted into the oxide and *vice versa*. The best value appears to be 24·32.

**342. Magnesium Oxide, Magnesia Usta, MgO.**—Magnesium oxide may be prepared by the combustion of magnesium,

$$2Mg + O_2 = 2MgO.$$

In commercial practice it is made by heating the native carbonate, magnesite,

$$MgCO_3 = MgO + CO_2,$$

or by calcining the hydroxide, made by the action of lime on magnesium chloride, a waste product in the potash industry,

$$Ca(OH)_2 + MgCl_2 = Mg(OH)_2 + CaCl_2$$
$$Mg(OH)_2 = MgO + H_2O.$$

Magnesium oxide is a white powder. It is highly infusible, but can be melted at the highest temperature of the oxyhydrogen flame. Magnesium oxide dissolves in about fifty thousand times its weight of water and the solution is alkaline.

It is a basic oxide, dissolving readily in acids to form magnesium salts. It is not reduced by hydrogen or carbon.

Magnesia is used in medicine. It neutralises an excess of acid in the stomach, if present, and the magnesium salts so formed have a laxative action. Large quantities of magnesia are used for making fire bricks for lining furnaces (cf. Fig. 187).

**343. Magnesium Hydroxide, $Mg(OH)_2$** is made by the action of potassium or sodium hydroxide upon a solution of a magnesium salt,

$$2KOH + MgCl_2 = Mg(OH)_2 + 2KCl.$$

Magnesium hydroxide forms a white powder only very slightly soluble in water but readily soluble in ammonium chloride solution.

The magnesium hydroxide in contact with water yields a small proportion of magnesium and hydroxyl ions. The combination of the latter with the ammonium ions, giving ammonium hydroxide and ammonia, causes the magnesium hydroxide to dissolve and dissociate, so restoring equilibrium. This process may continue until the magnesium hydroxide has dissolved.

(1) $$\underset{\text{Solid.}}{Mg(OH)_2} \rightleftharpoons Mg^{++} + 2OH^-$$

(2) $$NH_4^+ + OH^- \rightleftharpoons NH_4OH \rightleftharpoons NH_3 + H_2O.$$

Magnesium hydroxide is basic in character. It absorbs carbon dioxide from the air and has a slightly alkaline reaction.

It finds a use in the sugar industry, for when mixed with molasses, which contains sugar in a form not easily crystallisable, it produces insoluble magnesium saccharate, which can be decomposed by carbon dioxide, forming magnesium carbonate and pure sugar. Strontium hydroxide is commonly used for the same purpose.

**344. Magnesium Salts.**—Only one series of magnesium salts exists. They are colourless except when combined with a coloured acid, and have a bitter taste. They are not poisonous but have the

effect of saline purgatives. Magnesium compounds give no colour to the Bunsen flame.

Solutions of magnesium salts contain the ion $Mg^{++}$. They give precipitates with the following reagents :—

(1) Alkalis precipitate magnesium hydroxide, soluble in ammonium chloride solution,

$$Mg^{++} + 2OH^- \rightleftharpoons Mg(OH)_2\downarrow .$$

(2) Soluble carbonates precipitate basic magnesium carbonates (*q.v.*), also soluble in ammonium chloride.

The above precipitation reactions will not, of course, take place in a solution containing ammonium salts.

(3) Sodium phosphate in presence of ammonia and ammonium salts precipitates white crystalline magnesium ammonium phosphate

$$Mg^{++} + NH_4^+ + PO_4^{---} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O.$$

The salt is practically insoluble in water and even less soluble in ammonia. Its formation distinguishes magnesium from the alkali-metals and also affords a means of estimating magnesium (§350).

**345. Magnesium Chloride $MgCl_2$** is found in sea-water and also combined with potassium chloride as carnallite $KCl.MgCl_2.6H_2O$. It can be made by the usual methods for preparing soluble salts (§ 172), the hydrate $MgCl_2.6H_2O$ being obtained. If an attempt is made to dehydrate this by heat the chloride decomposes slightly,

$$MgCl_2 + H_2O \rightleftharpoons MgO + 2HCl.$$

The difficulty is overcome by dehydrating in a current of hydrogen chloride, the high concentration of this preventing the formation of magnesium oxide in appreciable quantity.

On the commercial scale magnesium chloride is made from the mother liquors from which potassium chloride has been crystallised (§ 265) in its manufacture from Stassfurt carnallite.

Hydrated magnesium chloride is a colourless deliquescent salt with a bitter taste. It is very soluble in water ; 100 gms. of water at room temperature dissolve 130 gms. of the chloride, and at 100° C. about 366 gms. It forms compounds with alcohols, such as

$$MgCl_2.6C_2H_5OH.$$

When heated the hydrated salt decomposes as mentioned above. The anhydrous salt, heated in a current of oxygen, is partially decomposed into magnesium oxide and chlorine.

$$2MgCl_2 + O_2 = 2MgO + 2Cl_2.$$

Concentrated magnesium chloride solution combines with mag-

nesium oxide to form the oxychloride. A cement is occasionally made by mixing magnesium oxide and magnesium chloride solution as above. It forms a paste which soon sets to a hard mass of the oxychloride, the composition of which approximates to $MgCl_2.5MgO$ *aq*.

*Magnesium bromide* $MgBr_2$ occurs in sea water, as also does the iodide.

**346. Magnesium Carbonate $MgCO_3$** is found native as *magnesite* and associated with calcium carbonate as *dolomite*. When sodium bicarbonate solution saturated with carbon dioxide is mixed with a solution of a magnesium salt the normal carbonate is slowly deposited. If, however, solutions of magnesium sulphate or chloride are mixed with solutions of sodium carbonate various *hydrated basic carbonates* are obtained. These occur in two forms. If precipitation is carried out in the cold a very bulky precipitate is obtained, which dries to a voluminous light powder, known as *magnesia alba levis*. Precipitation in boiling solution gives a denser form, *magnesia alba ponderosa*. The light variety is said to be $3MgCO_3.Mg(OH)_2.3H_2O$, and the heavy variety $3MgCO_3.Mg(OH)_2.4H_2O$.

It is, however, doubtful if these carbonates are pure compounds (*v*. § 567).

All the varieties of magnesium carbonate are white powders, insoluble in water. When heated they decompose, leaving magnesium oxide, *magnesia usta*.

Magnesium carbonate is insoluble in water, but soluble in carbon dioxide solution, forming the bicarbonate,

$$MgCO_3 + H_2CO_3 \rightleftharpoons Mg(HCO_3)_2.$$

It is also soluble in solutions of ammonium salts, the soluble double carbonate of magnesium and ammonium being formed. In other respects magnesium carbonate has the usual properties of carbonates.

**347. Magnesium Nitride $Mg_3N_2$** is formed when magnesium is heated in a current of nitrogen. It is also formed when the metal is heated in an insufficient supply of air. Thus, if a deep layer of magnesium powder is heated in a covered crucible for some time the upper part will be converted into oxide and the lower into nitride. Magnesium nitride forms a yellowish powder. Water decomposes it to magnesium hydroxide and ammonia,

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3.$$

**348. Magnesium Nitrate $Mg(NO_3)_2 . 6H_2O$** is a very soluble salt. Like the chloride it cannot be dehydrated without partial decomposition. In other respects it resembles the nitrates of the heavy metals (§ 750).

**349. Magnesium Sulphate $MgSO_4$.**—F. Hoffmann, in 1729, drew

attention to the existence of this salt in various mineral waters and considered it to be a compound of sulphuric acid and a 'calcareous earth.'

Magnesium sulphate occurs as the mineral *kieserite*, $MgSO_4.H_2O$, in the Stassfurt deposits, and as *epsomite* $MgSO_4.7H_2O$, in certain gypsum deposits. Many mineral springs contain the salt, such as those of Epsom (from which the term Epsom salts is applied to the hydrate $MgSO_4.7H_2O$), Bath, Seidlitz, etc.

Magnesium sulphate is generally manufactured from kieserite. This salt is soluble with great difficulty, and any other adherent salts are washed away from it with water. The kieserite slowly hydrates itself and sets to a solid mass of epsomite. This is recrystallised and sold as Epsom salts.

$$MgSO_4.H_2O + 6H_2O = MgSO_4.7H_2O.$$

Some magnesium sulphate is made from dolomite, which is calcined and treated with sulphuric acid. The supernatant solution of magnesium sulphate is siphoned from the insoluble calcium sulphate and crystallised.

Hydrated magnesium sulphate forms colourless crystals of composition $MgSO_4.7H_2O$. They have a harsh and bitter taste and act as an excellent mild purgative. They are freely soluble in water, 100 gms. of which dissolve 25·76 gms. at 0° C.

When heated the crystals lose six molecules of water at 100–150° C., but retain the seventh till 200° C. is reached (cf. § 208). In chemical behaviour magnesium sulphate has the usual properties associated with magnesium salts and sulphates.

**350. Detection and Estimation of Magnesium.**—Magnesium is detected in presence of other metals by the fact that in presence of ammonium salts it is not precipitated as sulphide, hydroxide or carbonate. It is thereby distinguished from all metals except the alkali metals. From these it is distinguished by its giving a crystalline precipitate of magnesium ammonium phosphate,

$$MgNH_4PO_4.6H_2O,$$

when a solution of a magnesium salt is mixed with solutions of ammonia, ammonium chloride and sodium phosphate.

To estimate magnesium the above phosphate may be precipitated, quantitatively filtered off, dried, ignited and weighed as pyrophosphate $Mg_2P_2O_7$.

$$2[MgNH_4PO_4.6H_2O] = Mg_2P_2O_7 + 2NH_3 + 13H_2O.$$

## CALCIUM Ca. 40·08

**351. Historical.**—Calcium carbonate in its various mineral forms

has, of course, been known since the earliest times, and lime-burning was practised by the Romans, and in all probability by earlier peoples. The relation between chalk, slaked lime and quick-lime was explained by Black as recently as 1756. The element calcium, in an impure state, was prepared in 1808 by Davy. Calcium was not obtained in a pure state until Moissan, in 1898, obtained it in a crystalline condition.

**352. Occurrence.**—The element calcium does not occur free in Nature, but its compounds form a considerable part of the earth's crust. Calcium carbonate as *calcite*, *marble*, *limestone* and *chalk* forms whole mountain ranges, while *dolomite*, calcium carbonate associated with magnesium carbonate, also occurs in enormous masses. Calcium sulphate in the forms of *anhydrite* $CaSO_4$, and *gypsum* $CaSO_4.2H_2O$, is a very common mineral. Calcium phosphate and fluoride also occur in large quantities, while calcium silicates form a constituent of many igneous rocks.

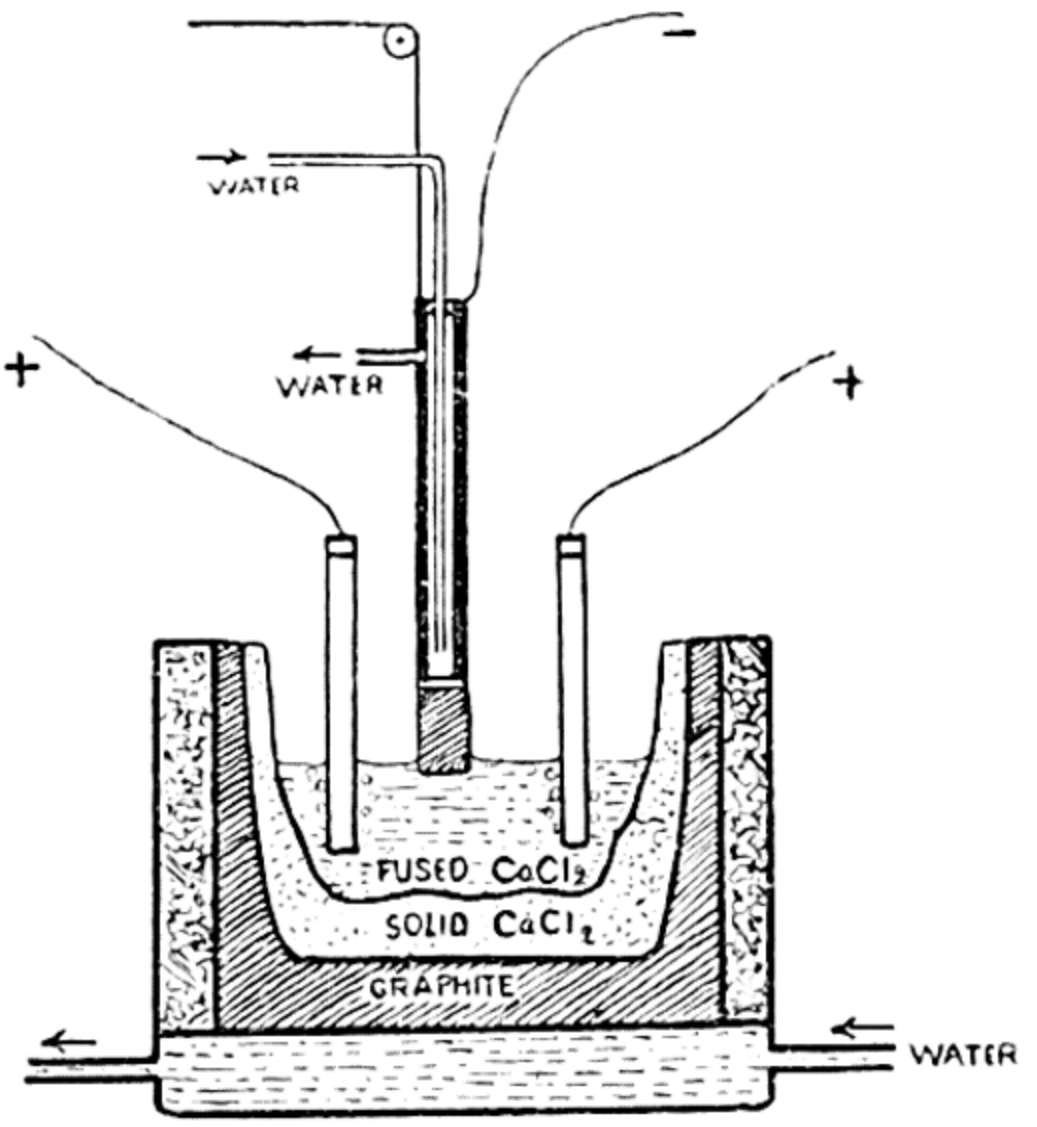


FIG. 85.—Preparation of calcium by electrolysis of fused calcium chloride.

Calcium salts are present in most natural waters. They are necessary constituents of both plant and animal tissues. The mineral portions of the bones consist of calcium phosphate, and calcium salts therefore play a very important part in the human body. While most articles of food contain an adequate supply of calcium compounds, the presence of a small proportion of vitamin D is needed to secure its absorption by the bowel. A deficiency of this vitamin therefore tends to produce the disease of rickets. The proportion of calcium present in the blood is regulated by special

glands, the parathyroids, a disordered functioning of which gives rise to several, fortunately rare, disorders.

**353. Preparation of Calcium.**—Calcium is commonly prepared by the electrolysis of fused calcium chloride.

$$CaCl_2 = Ca + Cl_2.$$

Several processes have been used and the most satisfactory appears to be that described below and illustrated in Fig. 85 :—

Pure fused calcium chloride, or a mixture of calcium chloride with 10 per cent. of the fluoride is used as the electrolyte. This is contained in a cell of graphite, which is protected by the chloride solidified upon it. The anodes are of graphite and the cathode is a water-cooled graphite rod. On this rod, which only just touches the surface, calcium solidifies and by slowly raising it a rod of calcium is produced. Chlorine is formed at the anodes and is allowed to pass away up a flue. Considerable care is needed in regulating the current, temperature, etc. A voltage of 25–30 with a current of *c.* 400–500 amp. per cell is employed.

**354. Properties.**—Calcium is a silver-white metal harder than lead but softer than the majority of the metals. It melts at 810° C. Calcium is very light, having a density of 1·55.

Calcium dissolves in melted sodium, crystallising out on cooling. The excess of sodium may be removed by treatment with alcohol, leaving almost pure crystals of calcium.

Calcium is very reactive in character. It combines directly with most of the non-metallic elements.

Thus it burns in air or oxygen with a reddish light, forming the oxide. In air some nitride is also formed,

$$O_2 + 2Ca = 2CaO.$$

Calcium reacts rapidly with nitrogen at about 400° C. and the ready formation of the nitride affords an excellent method of separating nitrogen from the rare gases (§ 1241).

$$3Ca + N_2 = Ca_3N_2.$$

Calcium reacts with hydrogen under pressure to form the hydride $CaH_2$. Calcium burns when heated in chlorine, bromine and iodine, forming the halides (*q.v.*). Calcium reacts with water slowly, giving calcium hydroxide and hydrogen, $Ca + 2H_2O = Ca(OH)_2 + H_2$. It affords an efficient means of removing water from alcohol. Acids attack it strongly, producing calcium salts and hydrogen.

**355. Atomic Weight of Calcium.**—The best determinations of the atomic weight of calcium, for which the approximate value (determined from Dulong and Petit's law, the Periodic law, molecular weights of calcium salts in solution, etc.) is 40, are derived from :—

(1) The conversion of the pure Iceland spar, $CaCO_3$, into calcium oxide

CaO. (2) The change of weight on conversion of calcium chloride $CaCl_2$ into silver chloride 2AgCl. The results indicate a value of 20·04 for the equivalent or 40·08 for the atomic weight. Isotopes of mass 40 and 44 are known. and, possibly, minute traces of the isotope 41, derived from the radioactive decomposition of potassium.

### The Oxides and Hydroxides of Calcium

Calcium has three oxides, only one of which is of importance. They are :—

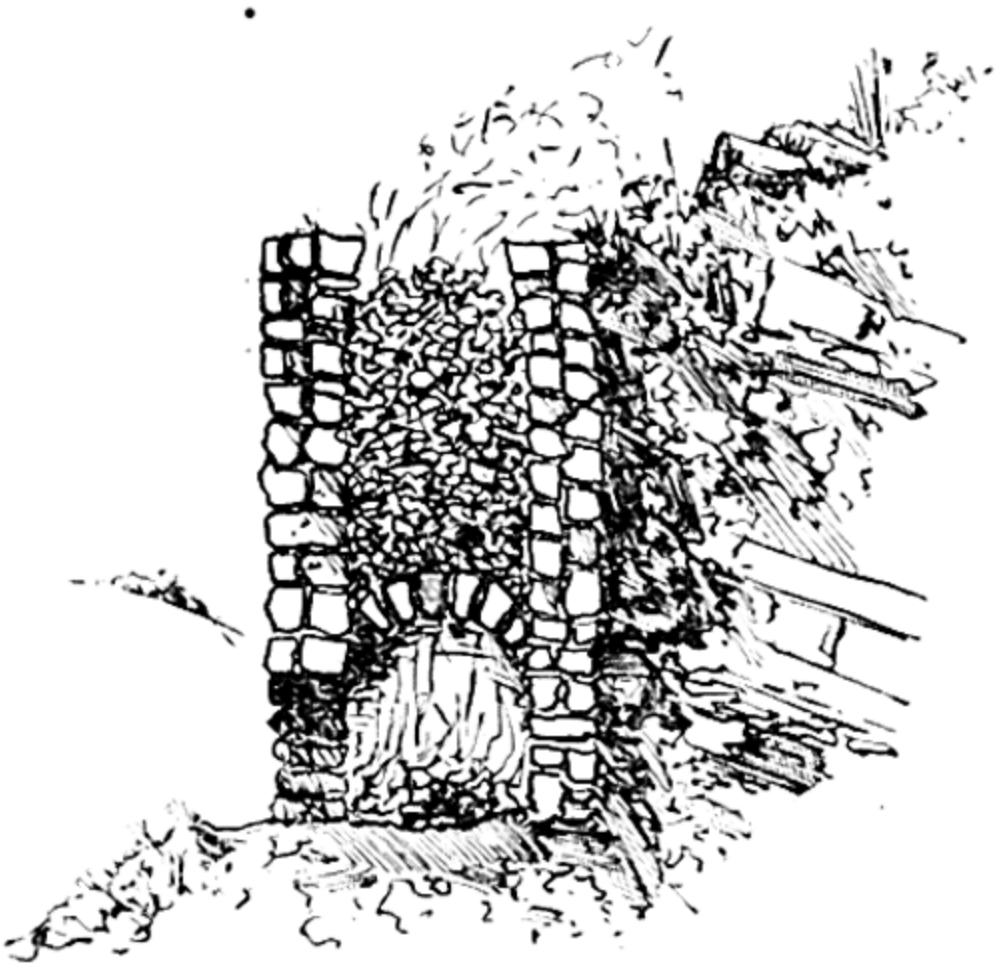

Fig. 86.—Flare kiln.

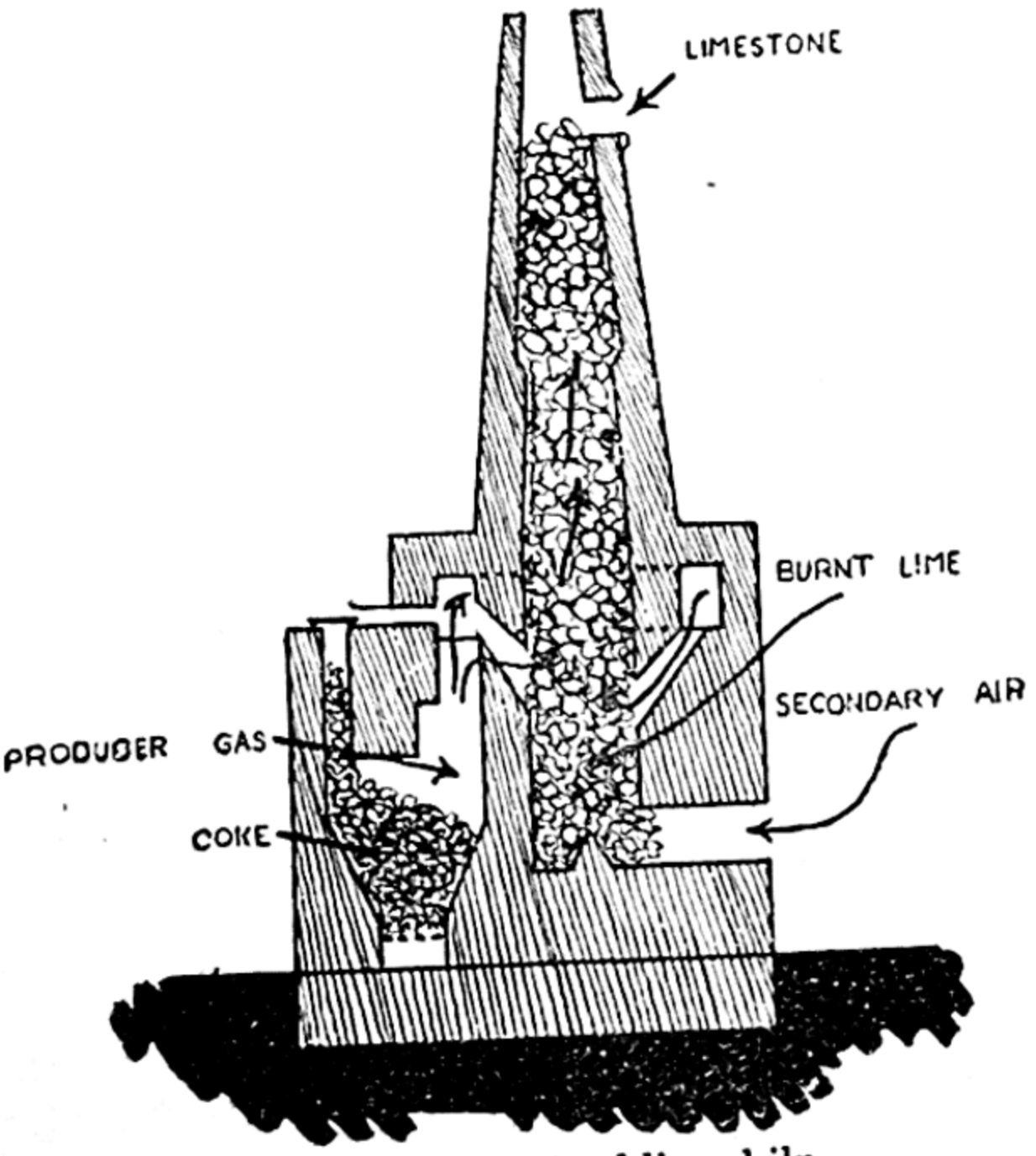


Fig. 87.—Gas-fired lime-kiln

| | |
|---|---|
| Calcium oxide, quicklime . . . | $CaO$ |
| Calcium peroxide . . . . . | $CaO_2$ |
| Calcium tetroxide . . . . . | $CaO_4$ |

**356. Manufacture of Lime.**—Quicklime is ordinarily obtained by heating calcium carbonate. The action is reversible,

$$CaCO_3 \rightleftharpoons CaO + CO_2,$$

and does not complete itself unless the carbon dioxide is allowed to escape.

According to the Phase Rule, § 87, we have here three phases, $CaO$, $CaCO_3$, $CO_2$, and two components, calcium oxide and carbon dioxide. The system is therefore univariant and to each temperature corresponds a fixed concentration of carbon dioxide. Thus at each temperature a certain partial pressure of carbon dioxide represents the concentration necessary to preserve equilibrium. At 500° C. calcium carbonate is in equilibrium with 0·11 mm. pressure of $CO_2$; at 600° C., 2·35 mm. pressure; and at about 890° C., 760 mm.

If these pressures are exceeded the lime and carbon dioxide recombine; if they are not reached carbon dioxide will escape and dissociation will proceed.

In practice, therefore, any degree of heat above, say, 525° C. will cause calcium carbonate to decompose, provided the carbon dioxide formed is continually carried away. Above 890° C., when the partial pressure exceeds that of the atmosphere calcium carbonate will decompose completely unless confined under pressure.

In practice, a temperature of about 800–1,000° C. is used. This temperature is not reached in a crucible heated by a Bunsen burner, and to decompose calcium carbonate under laboratory conditions the use of the Méker burner (p. 458) or blow-pipe is required.

On the large scale calcium carbonate is heated in kilns.

The simplest type is the flare kiln (Fig. 86). The illustration explains itself. The limestone or chalk reaches a temperature of 1,000° C. in parts, the carbon dioxide being carried away through the top of the kiln. These simple kilns are wasteful of fuel but very cheap to construct. They are much used where comparatively small quantities of lime are wanted at intervals.

Many more complicated types of kiln have been used. The type illustrated in Fig. 87 burns producer gas generated from coke. Limestone is fed in at the top and lime raked out at the bottom. The process is thus a continuous one. For laboratory purposes very pure lime is sold which is made by heating marble, a very pure form of calcium carbonate.

**357. Properties of Calcium Oxide.**—Calcium oxide is usually met with as hard white masses. It can be crystallised after fusion in the electric furnace. Its melting point is about 2,570° C It is volatile at temperatures below its melting point. Its high fusing point was utilised in the now almost obsolete 'lime-light,' in which a cylinder

of lime was heated to brilliant incandescence by an oxyhydrogen or oxy-coal gas flame. At this temperature (*c.* 1,500° C.) the lime volatilises appreciably.

Calcium oxide is a reactive substance at high temperatures, most of the non-metals, including the halogens and sulphur, reacting with it above 300° C. Fluorine reacts in the cold.

Calcium oxide reacts vigorously with water, much heat being evolved, and calcium hydroxide being formed as a white powder.

$$CaO + H_2O = Ca(OH)_2.$$

This property makes quicklime useful as a drying agent in cases where the more rapidly-acting calcium chloride or sulphuric acid cannot be used. Thus ammonia gas is dried in this way (§ 691), and alcohol is commonly dehydrated by being kept standing over quicklime.

Calcium oxide does not react in the cold with most acid gases, such as carbon dioxide, sulphur dioxide and hydrogen chloride ; but when heated it reacts with them, forming the appropriate calcium salt.

It reacts with acids in solution, probably 'slaking' to calcium hydroxide, which then reacts with the acid.

Quicklime finds its chief use in the preparation of slaked lime for building purposes. Quicklime can be preserved in dry air indefinitely, since it does not react with carbon dioxide. Slaked lime, however, soon becomes transformed into carbonate. Builders therefore prefer to buy quicklime and slake it whenever they wish to make mortar or plaster.

Limes of various qualities are distinguished by the trade. A 'fat' lime is a pure lime, which slakes readily. A 'poor' lime contains some silica or alumina and slakes slowly. The latter has, in a small degree, some of the properties of a cement.

**358. Calcium Hydroxide, Slaked Lime, $Ca(OH)_2$.**—This substance is obtained by the action of quicklime on water (*v. supra*, § 357), or by the action of caustic alkalis on a soluble calcium salt.

It is a white amorphous powder, sparingly soluble in water. Its solubility diminishes as the temperature rises, as shown by the solubility diagram illustrated in Fig. 24.

When calcium hydroxide is heated it decomposes, yielding calcium oxide. The action begins at about 360° C., and is rapid at a red heat.

$$Ca(OH)_2 = CaO + H_2O.$$

Calcium hydroxide has the usual properties of alkalis and exhibits the same reactions as caustic soda and caustic potash in a lesser degree.

It reacts very readily with acids and acid gases, forming calcium salts. A mixture of calcium hydroxide and sodium hydroxide,

obtained by slaking lime with caustic soda, is known as *soda-lime*, and is a particularly efficient absorbent of acid gases, acidic anhydrides, the halogens, etc. Among these we number carbonyl chloride, hydrogen sulphide, hydrogen chloride, bromide and iodide, sulphur dioxide, carbon dioxide, nitrogen peroxide, chlorine, bromine vapour, etc. On account of this property it was used in gas-masks during the war of 1914–1918.

These contained a layer of absorbent charcoal (§ 530), which absorbed many neutral organic substances, and a mixture of sodium permanganate and soda-lime, the former reacting with any reducing gas and the latter absorbing chlorine or any acid gas. Modern gas-masks rely on activated charcoal alone.

In the purification of coal gas, carbon dioxide, hydrogen sulphide, and carbon disulphide are sometimes removed by absorption with lime.

The chief use of lime in industry is in the making of mortar and plaster.[1] Mortar consists of lime, sand and water, and plaster consists of lime and water, together with some cow's hair to give greater strength.

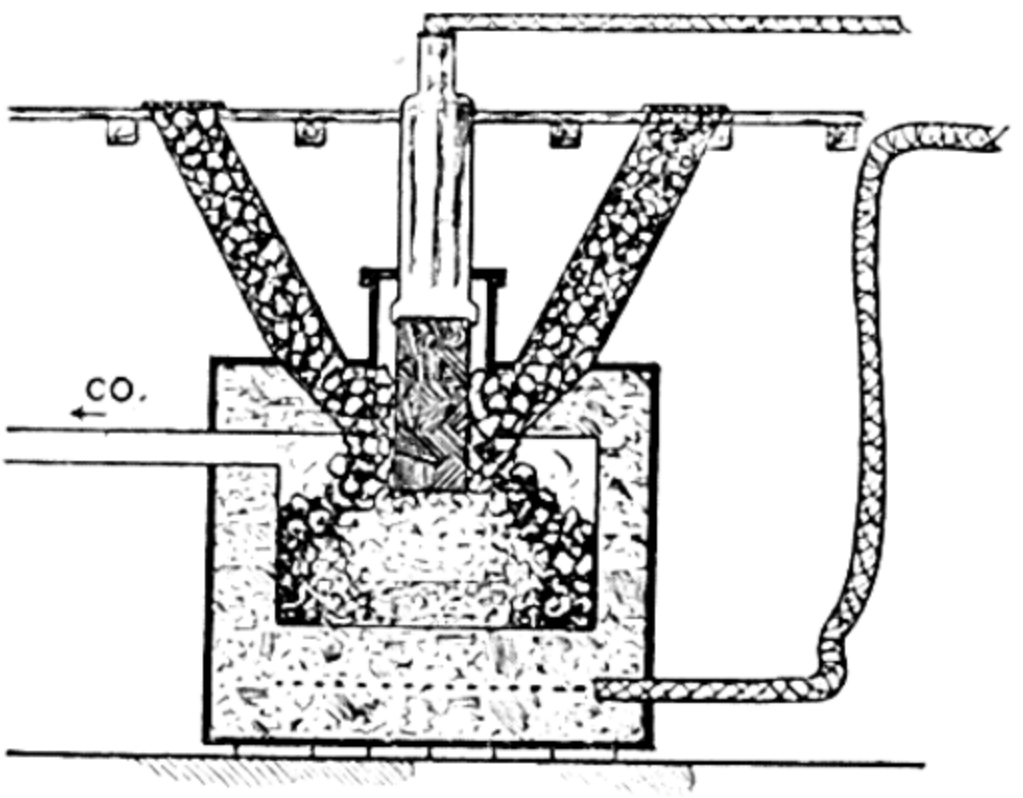


FIG. 88.—Manufacture of calcium carbide.

The setting of mortar and plaster is first due simply to drying out of the water. This action is followed by conversion of the outermost layer into calcium carbonate, but even in Roman buildings the whole of the lime of the mortar has not yet been converted into carbonate. Lime finds numerous uses in the chemical industries, among which we may note the preparation of bleaching powder (§ 1066), and of ammonia (§ 690).

*Calcium peroxide* $CaO_2$, may be made by the action of hydrogen peroxide on lime-water, the octahydrate $CaO_2.8H_2O$ being precipitated. It resembles barium peroxide (*q.v.*), but is less stable.

*Calcium tetroxide* $CaO_4$ is made by heating the hydrated peroxide with 30 per cent. hydrogen peroxide. It is a yellow powder which, when treated with acids, gives hydrogen peroxide and oxygen. It is analogous in behaviour to potassium peroxide $KO_3$.

## SALTS OF CALCIUM

**359. General Properties of Calcium Salts.**—Calcium salts are white

[1] Not plaster of Paris (*v.* p. 347).

and give colourless solutions, unless the acid radical is one with which colour is associated. These solutions contain the colourless ion, $Ca^{++}$.

Calcium compounds in general are not poisonous unless the acid radical has deleterious properties

Solutions of calcium salts give precipitates with a large number of acid radicals. Most of these precipitates are only produced in neutral or alkaline solution.

*In Acid Solution.*—The sulphate and fluoride of calcium are precipitated when soluble fluorides or sulphates are mixed with moderately acid solutions of calcium salts. The sulphate is sparingly soluble (*c.* 1 : 250) and is therefore only precipitated from fairly strong solutions.

*In Neutral Solution* precipitates of the calcium salt are produced by a number of salts, including the above, and also sulphites, phosphites, pyrophosphates, orthophosphates, arsenites, arsenates, silicates, borates, ferrocyanides, and the salts of many organic acids, including oxalates and tartrates.

**360. Calcium Hydride $CaH_2$** is made by passing hydrogen over melted calcium. Its use in the preparation of hydrogen is referred to in § 185.

**361. Calcium Borates** are found as native minerals. They have been utilised as sources of borax and boric acid (§ 467).

**362. Calcium Carbide $CaC_2$.**—This substance is made on the large scale by the action of coke on lime at the high temperatures attainable in the electric furnace,

$$CaO + 3C = CaC_2 + CO.$$

The coke and lime are charged through hoppers into a furnace containing a large carbon anode. The cathode is the carbon lining of the floor. The current arcing from one piece of coke to the next causes the material to react and the calcium carbide formed to liquefy.

Calcium carbide is white when pure, but the commercial product is grey or black. When treated with water it forms lime and acetylene,

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

The reaction and the methods of purifying the gas so obtained are further described in § 544.

Heated in nitrogen, calcium carbide forms calcium cyanamide (§ 366) and free carbon,

$$CaC_2 + N_2 = CaCN_2 + C.$$

**363. Calcium Acetate $Ca(C_2H_3O_2)_2$** has a commercial importance, being made in large quantities from the impure dilute acetic acid obtained by the distillation of wood. It is converted into acetic acid by distillation with sulphuric acid or into *acetone* by dry distillation :

$$Ca\begin{<}OOC\,.\,CH_3\\OOC\,.\,CH_3\end{>} = CaCO_3 + \begin{<}CH_3\\CH_3\end{>}CO.$$

**364. Calcium Oxalate $CaC_2O_4$** is very sparingly soluble and may accordingly be used for the determination of calcium (*v.* p. 345). It is soluble in mineral acids.

**365. Calcium Carbonate $CaCO_3$.**—This extremely abundant and important substance occurs in many different forms. Two varieties of different crystalline form are known :—

(1) *Calcite.*—Hexagonal crystals, doubly refractory, marked cleavage.

(2) *Aragonite.*—Rhombic crystals.

Calcite is the stable form at ordinary temperature.

Aragonite is probably the stable form below — 43° C. Dry aragonite is, however, transformed into calcite so slowly, if at all, at ordinary temperatures that it may be preserved indefinitely. It rapidly becomes transformed into calcite at 400°–500° C., and in the moist state the change takes place at ordinary temperatures.

Calcium carbonate, crystallised as calcite, is found in a variety of mineral forms.

*Iceland spar* is pure colourless calcite, *calc spar* or *calcite* being often white and opaque. *Marble* is a mass of small crystals of calcite, while *limestone* is a wide term covering a variety of minerals consisting mainly of calcium carbonate. *Chalk* appears to the naked eye to be amorphous. Microscopic examination shows it to consist of the shells of microscopic foraminifera, and these shells are probably composed of calcite.

*Preparation.*—The native forms of calcium carbonate, Iceland spar and marble, are often used in the laboratory, the former being useful where material of the highest purity is required.

Calcium carbonate is also prepared as a white powder, known as *precipitated chalk*, by dissolving marble in hydrochloric acid and adding ammonia to precipitate any iron, aluminium, etc., present. The liquid is filtered, and the calcium carbonate precipitated by addition of ammonium carbonate, then washed and dried,

$$Ca^{++} + CO_3^{--} \rightleftharpoons CaCO_3$$

*Properties.*—Calcium carbonate forms colourless hexagonal crystals of calcite (Plate X.), or rhombic crystals of aragonite, or a white, apparently amorphous, powder. Calcite or Iceland spar

is commonly met with as cleavage fragments in the form of parallelopipeds.

The density of calcite is 2·715. When heated at atmospheric pressure calcium carbonate decomposes (§ 356), but when heated in carbon dioxide under 1,050 atmospheres pressure it fuses at 1,340° C.

Calcium carbonate is almost insoluble in water (about 0·0018 gm. per 100 gms. water). In presence of carbon dioxide the soluble calcium bicarbonate is produced,

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca(HCO_3)_2,$$

and it is thus possible to dissolve as much as 2·29 gm. of calcium carbonate in a litre of water.

The behaviour of calcium carbonate and bicarbonate, in presence of water, is discussed under the heading of Water, § 200.

When calcium carbonate is heated it decomposes to the oxide and carbon dioxide. This reaction is discussed in § 356. In other respects it has the usual properties of a carbonate (§ 567).

*Calcium bicarbonate* $Ca(HCO_3)_2$ occurs in the solutions formed by the action of carbon dioxide and water upon calcium carbonate. It can be prepared in an impure state by the action of ammonium

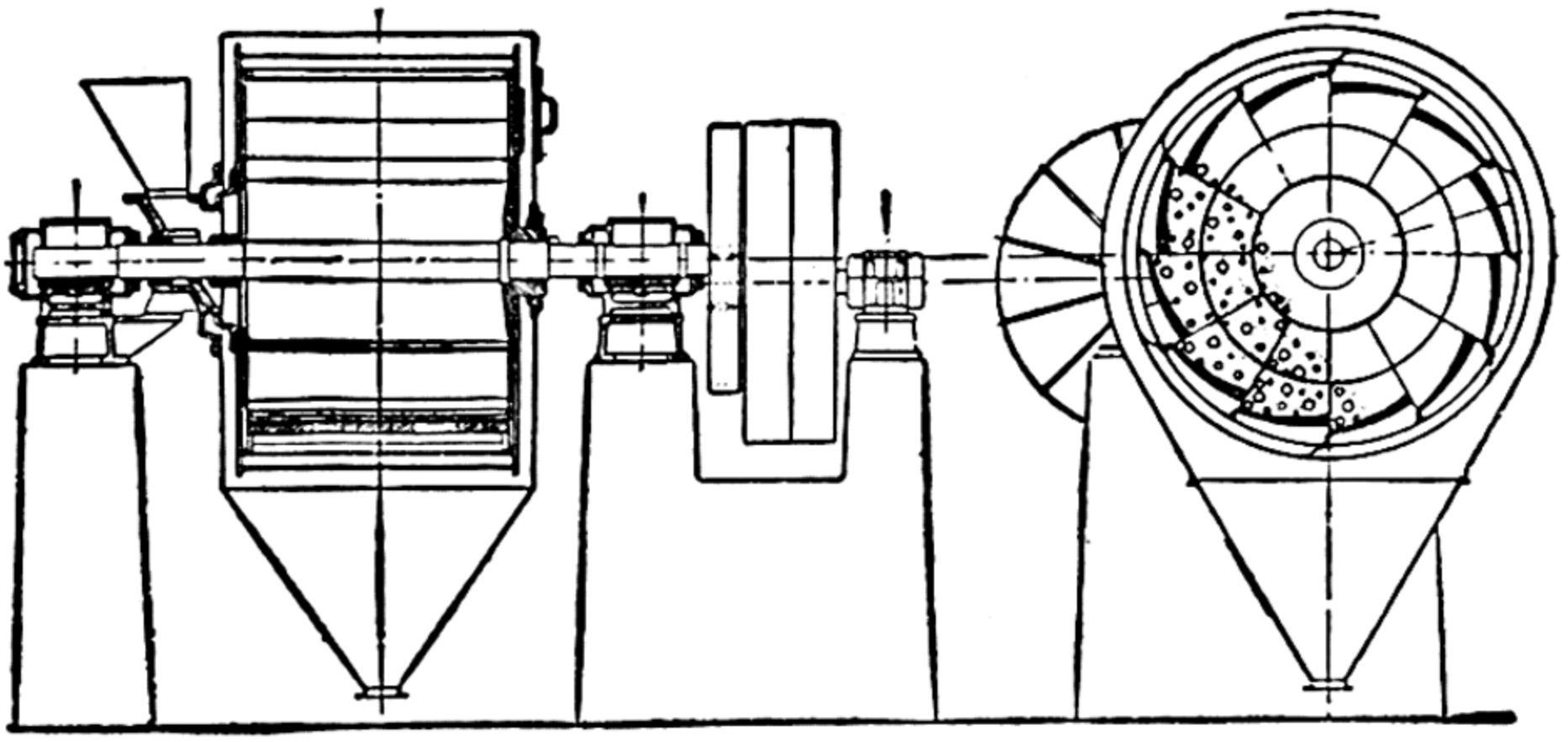

FIG. 88B.—Ball-mill for grinding cement clinker.

bicarbonate on calcium chloride, both solutions being kept at 0° C.

**366. Calcium Cyanamide** is made on the large scale by the action of nitrogen (obtained by the air-liquefaction process) on red-hot calcium carbide. The latter substance is heated in an atmosphere of nitrogen, which is absorbed at about 800° C., forming calcium cyanamide,

$$CaC_2 + N_2 = CaCN_2 + C.$$

Calcium cyanamide has been used as an artificial manure, for when dug into the soil it is decomposed, giving calcium carbonate and cyanamide, which further decomposes, giving urea. This latter substance is converted into ammonium carbonate and ultimately to nitrates by the bacteria of the soil,

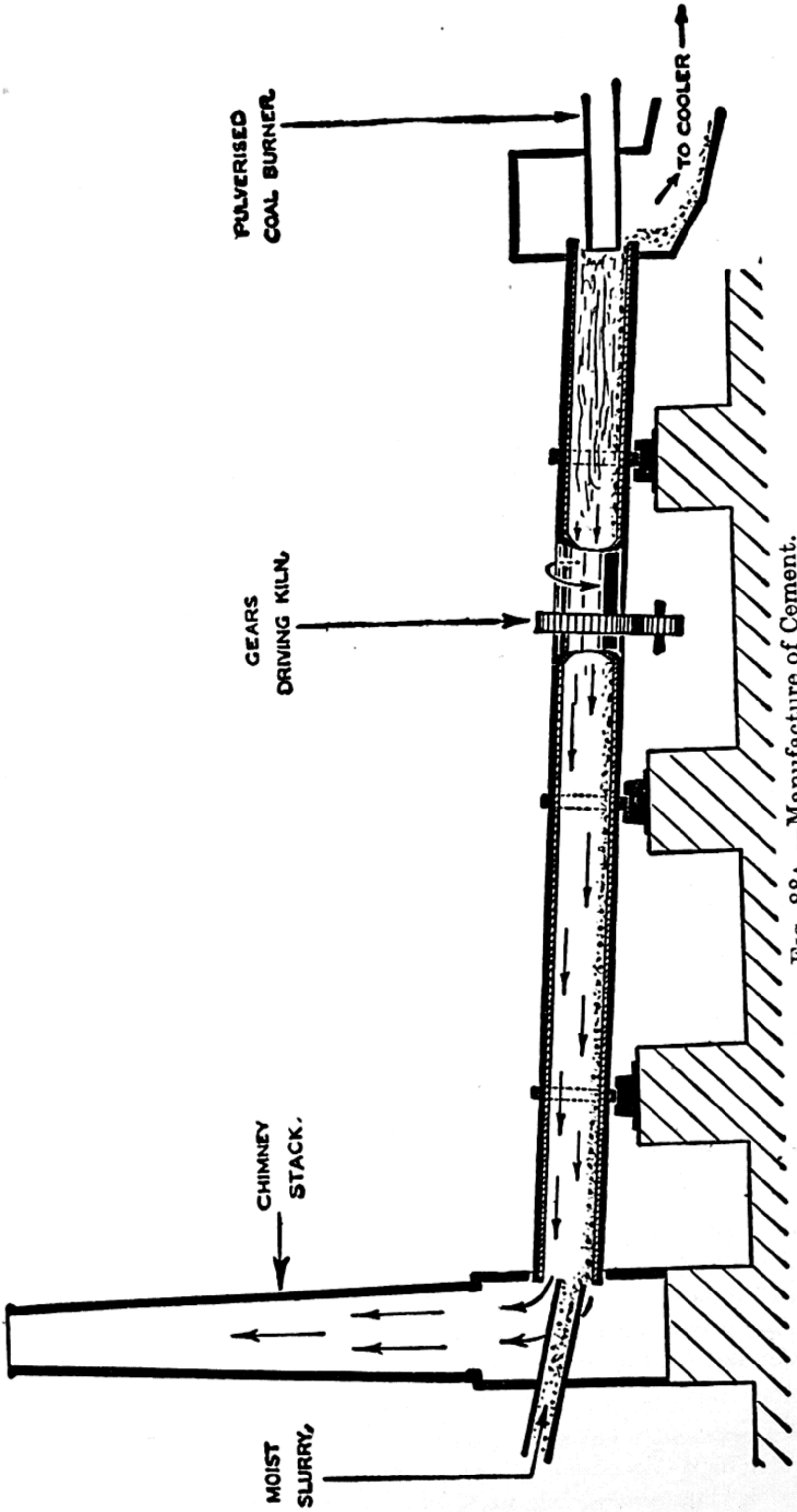


FIG. 88A.—Manufacture of Cement.

$$CaN.CN + H_2O + CO_2 = CaCO_3 + H_2N.CN.$$
$$H_2N.CN + H_2O = CO(NH_2)_2.$$

It is also used in the manufacture of cyanides and ammonia.

**367. Calcium Silicate $CaSiO_3$** occurs in Nature. Calcium silicates form a large part of glasses (*q.v.*, § 600) and slags. It is also contained in Portland cement.

**368. Portland Cement.**—Cement is the characteristic building material of the twentieth century, and its manufacture is a gigantic industry. The materials from which cement is made are clay and chalk. Sometimes these are found ready mixed as 'marl,' more often they are separately quarried. These materials are ground with water so as to make a thin mud or 'slurry.' This mud is fed into a rotary kiln, a huge cylinder as big as a factory chimney, 8–14 feet wide and from 150 to 350 feet long. It is gently sloped and slowly rotates so that the slurry works its way from the top to the bottom. Into the bottom end a huge flame 40 or 50 feet in length is driven by a pulverised coal burner. The hot end of the kiln may be at 1,500° C. This roasts the chalk and clay to cement clinker, which emerges as hard stony pebbles as big as marbles. It is now cooled and then ground, usually in a tube mill, a strong steel cylinder partly filled with steel balls, which falling one over the other rapidly reduce the clinker to fine dust (95 per cent. to pass 170-mesh sieve).

Portland cement contains tricalcium silicate $Ca_3SiO_5$ and calcium aluminate $Ca_2Al_2O_5$, together with other compounds of lime, silica, alumina and iron.

The setting of cement does not appear to be only a process of hydration analogous to the setting of plaster of Paris, but at the same time involves the decomposition of the above compounds and the formation of several others. These include calcium hydroxide, tricalcium aluminium silicate and calcium monosilicate, which are present both as crystals and in colloidal masses. The process is too complex for any equation to describe adequately the reactions which occur.

**369. Calcium Nitride $Ca_3N_2$** is prepared by heating calcium in a current of nitrogen at about 440° C.

It reacts with water, giving calcium hydroxide and ammonia,

$$Ca_3N_2 + 6H_2O = 3Ca(OH)_2 + 2NH_3.$$

**370. Calcium Nitrate $Ca(NO_3)_2$** is occasionally found in the soil as a product of the action of nitrifying bacteria (§ 674). It is made by the usual methods of preparing nitrates and also by the synthetic nitrate process described in § 737. It is occasionally known as 'air saltpetre.'

Calcium nitrate forms several hydrates; the one usually met with

is the tetrahydrate $Ca(NO_3)_2.4H_2O$, stable below 42·7° C. The salt is very hygroscopic.

It has the usual properties of a nitrate and has found some use as a fertiliser.

**371. Calcium Phosphide $Ca_3P_2$** may be made by fusing calcium with phosphorus in an inert atmosphere. It is at once decomposed by water, giving spontaneously inflammable phosphine (§ 770),

$$Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3.$$

**372. Calcium Phosphates.**—The phosphates of calcium are of great importance as fertilisers. They include :—

| | |
|---|---|
| Tricalcium orthophosphate . . | $Ca_3(PO_4)_2$ |
| Dicalcium orthophosphate . . | $CaHPO_4$ |
| Monocalcium orthophosphate . | $Ca(H_2PO_4)_2$ |

*Tricalcium orthophosphate* occurs native as *apatite*, usually associated with chloride and fluoride. It is found in many parts of the world, notably Florida, North Africa, France, Belgium, and the Pacific Islands. Tricalcium phosphate is the mineral constituent of bones.

It is readily obtained by the addition of a soluble phosphate in alkaline solution to a soluble calcium salt,

$$2Na_2HPO_4 + 2NH_4OH + 2CaCl_2 = 4NaCl + 2NH_4Cl + Ca_3(PO_4)_2 + 2H_2O$$

or,
$$HPO_4^{--} + OH^- = PO_4^{---} + H_2O$$
$$3Ca^{++} + 2PO_4^{---} = Ca_3(PO_4)_2\downarrow.$$

Calcium phosphate forms a white powder insoluble in water and unaffected by heat.

It is soluble in acids, but on addition of alkali it is reprecipitated,

$$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{++} + 2PO_4^{---}$$
Solid.
$$PO_4^{---} + H^+ \rightleftharpoons HPO_4^{--}$$
$$HPO_4^{--} + H^+ \rightleftharpoons H_2PO_4^-$$
$$H_2PO_4^- + H^+ \rightleftharpoons H_3PO_4.$$

The addition of hydrion removes the $PO_4^{---}$ ion and so causes the salt to dissolve. On addition of alkali to this solution hydrion is removed and consequently $PO_4^{---}$ is formed, and calcium phosphate reprecipitated. This is the reason why calcium and certain other phosphates are precipitated in qualitative analysis when ammonia is added (Group III. in most systems). The difficulty is got over by precipitating all the phosphate in nearly neutral solution as ferric phosphate and filtering this off.

Calcium phosphate is used for making phosphoric acid and phosphorus (*q.v.*), and also in the manufacture of superphosphate (*v. infra*).

*Dicalcium orthophosphate* $CaHPO_4$ is obtained by precipitating an acid solution of a calcium salt with sodium phosphate,

$$Na_2HPO_4 \rightleftharpoons 2Na^+ + HPO_4^{--}$$
$$Ca^{++} + HPO_4^{--} \rightleftharpoons CaHPO_4.$$

It is insoluble in water.

*Monocalcium orthophosphate* $Ca(H_2PO_4)_2.H_2O$ is made by the action of phosphoric acid on tricalcium phosphate,

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2.$$

It is soluble in water, thereby differing from the other phosphates, but unless excess of phosphoric acid is present it reverts to $CaHPO_4$,

$$3Ca(H_2PO_4)_2 \rightleftharpoons 3CaHPO_4 + 3H_3PO_4.$$

Calcium pyrophosphate and metaphosphate are known.

*Calcium Phosphate as a Fertiliser.*—The value of phosphorus in the soil is explained in § 760. Tricalcium phosphate is a valuable fertiliser, but is slow in action owing to its very small solubility. It is often used in the form of bone-meal, etc.

To obtain a quick-acting fertiliser, calcium phosphate is treated with crude sulphuric acid, when a product known as *superphosphate of lime* is obtained. This contains monocalcium orthophosphate, phosphoric acid, and calcium sulphate,

$$5Ca_3(PO_4)_2 + 11H_2SO_4 = 4Ca(H_2PO_4)_2 + 2H_3PO_4 + 11CaSO_4.$$

It is used in vast quantities and about 40 per cent. of the sulphuric acid made is used for this purpose.

The phosphorus in this product is in a soluble form, at once available to plants.

*Basic slag* (§ 1142), obtained in the basic Bessemer process, contains calcium phosphate, probably as calcium silicophosphate,

$$Ca_3(PO_4)_2.CaSiO_3.$$

When finely ground it is a valuable fertiliser.

**373. Calcium Sulphide CaS.**—This substance is prepared by heating lime in hydrogen sulphide, or by the reduction of calcium sulphate with carbon, or by the action of sulphur upon quicklime,

$$Ca(OH)_2 + H_2S = CaS + 2H_2O,$$
$$CaSO_4 + 2C = CaS + 2CO_2,$$
$$2CaO + 3S = 2CaS + SO_2.$$

It has been produced in vast quantities as a waste product in the Leblanc soda process, and forms the heaps of 'alkali waste' which form unsightly landmarks where this process is carried on.

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Calcium sulphide is a white powder, odourless in absence of moisture. It has a remarkably brilliant phosphorescence only equalled by zinc sulphide. Pure calcium sulphide has no phosphorescence, and the luminous sulphide always contains a minute amount of metallic impurity, say 0·01 per cent. of bismuth (manganese, copper, tungsten, etc.), and a small proportion, say 2 per cent., of the chloride of an alkali metal.

It has been supposed that the metallic impurities are converted into sulphides, which are in solid solution in the calcium sulphide. The illumination of the particles of these sulphides causes electrons to be emitted, and these gradually recombine with the atoms, producing phosphorescence.

A good specimen of the phosphorescent sulphide is hard to prepare by ordinary laboratory methods. Lime may be moistened with methylated spirit, containing a trace of bismuth nitrate. When dry it is mixed with an excess of sulphur and a little starch and a little sodium chloride, and heated to bright redness in a covered crucible. The quality of the lime is important, and that prepared by ignition of oyster shells is said to be best. After exposure to light the product emits a violet glow which gradually diminishes in intensity and finally fades out completely after some hours.

Calcium sulphide is sparingly soluble in water and is hydrolysed

$$2CaS + 2H_2O \rightleftharpoons Ca(OH)_2 + Ca(SH)_2$$

forming the hydrosulphide.

In other respects calcium sulphide has the usual properties of a sulphide (§ 905).

*Calcium hydrogen sulphide* $Ca(HS)_2$ is formed by the action of hydrogen sulphide on milk of lime,

$$Ca(OH)_2 + 2H_2S = Ca(SH)_2 + 2H_2O.$$

Calcium sulphide is a constituent of most of the depilatories sold for removing superfluous hair. It is also used in tanning for removing the hair from ox-hides.

**374. Calcium Polysulphides $CaS_n$.**—When lime is boiled with sulphur a mixture of calcium sulphide and thiosulphate is produced.

The yellow liquid so obtained was known to the late Egyptian and Greek alchemists as $\theta\epsilon\hat{\iota}o\nu$ $\ddot{\upsilon}\delta\omega\rho$, ***theion hudor***, the divine (or sulphurous—$\theta\epsilon\hat{\iota}o\nu$ has both meanings) water. They used it to attack various metals, which it did more efficiently than any substance then known, converting them into sulphides.

The liquid probably contains sulphides of formula $CaS_2$ to $CaS_7$ (*v.* § 906).

**375. Calcium Bisulphite $Ca(HSO_3)_2$,** made by passing sulphur dioxide into milk of lime, is used for bleaching paper pulp and as an antiseptic in the brewing industry.

**376. Calcium Sulphate $CaSO_4$.**—This substance occurs native, as *anhydrite* $CaSO_4$, and gypsum $CaSO_4.2H_2O$. The latter often occurs finely crystallised, and is then called selenite. A crystalline variety is known as *alabaster*, a name, however, occasionally applied to a translucent variety of calcium carbonate.

*Preparation.*—Calcium sulphate dihydrate may be prepared by the action of soluble sulphates on soluble calcium salts, or by the action of dilute sulphuric acid on calcium carbonate or hydroxide.

*Plaster of Paris.*—Gypsum, when heated to 100–200° C., is partially dehydrated and is converted into plaster of Paris; this is commonly said to be the hemihydrate but may not be a definite compound.

$$2CaSO_4.2H_2O = (CaSO_4)_2.H_2O + 3H_2O.$$

On the large scale gypsum is heated in large steel pots, holding several tons and provided with mechanical stirrers. It may also be heated in a rotary kiln in a similar manner to cement (§ 368).

The hemihydrate so obtained, when mixed with water, sets, in about five minutes, to a hard mass, expanding at the same time in such a way as to fill a mould very completely, and so produce a fine impression. Heat is produced at the same time. The setting is due to the formation of an interlacing mass of needles of gypsum.

If the gypsum be heated to a higher temperature than that needed to make plaster of Paris, but not to a very high temperature, a plaster is obtained which sets very much more slowly, forming a hard and resistant surface suitable for floors, etc. Still stronger heating destroys the setting properties altogether.

Calcium sulphate forms a white powder, slightly soluble in water (0·26 gm. $CaSO_4.2H_2O$ per 100 gms. water at 15° C.). It is not decomposed by heat. It has the properties of sulphates (§ 938).

*Uses.*—As plaster of Paris or flooring plaster, calcium sulphate is used in many types of cement and wall plaster. Keene's cement is a harder and more slowly-setting cement, made by heating gypsum to redness, moistening the product with alum solution, and again heating to redness. It is used for finishing corners of interior walls, etc., where a harder plaster is needed. Artificial marble is often made from plaster of Paris. It is also used for making various types of moulds for casting metal and for making casts for statuary. Bandages saturated with wet plaster of Paris are applied in surgical work in order to maintain parts of the body in a fixed position. The use of plaster bandages in the treatment of war wounds has recently gained favour.

Anhydrite has assumed considerable importance as a service of the sulphate ion. Thus ammonium sulphate is made industrially

by causing ammonium bicarbonate from the Solvay process to react with anhydrite. This enables the use of the relatively expensive sulphuric acid to be avoided.

**377. Calcium Chromate $CaCrO_4$.**—This salt is of interest as being much more soluble in water than barium or strontium chromates; a method of separating calcium from barium and strontium has been based on this fact.

**378. Calcium Fluoride $CaF_2$.**—This substance is found native as *fluorite* or *fluorspar*. The mineral forms cubic crystals, occasionally transparent but usually translucent, and often richly coloured. The name 'Blue John' is given to a blue variety used for ornamental vases, etc.

Calcium fluoride may be precipitated by the addition of a soluble fluoride to a solution of a calcium salt. It may also be made by the action of hydrofluoric acid on calcium oxide or carbonate.

The mineral is one of the chief sources of fluorine compounds (*q.v.*). The somewhat rare transparent specimens are used in optical work. The very low refractive index and weak colour dispersion of fluorite make it useful for small telescope and microscope lenses. It is also transparent to infra-red and ultra-violet rays. The coarser varieties are used as a flux in metallurgy.

**379. Calcium Chloride $CaCl_2$.**—Calcium chloride is present in sea water.

*Preparation.*—Calcium chloride is a waste product in the ammonia-soda process, and it has been difficult to find a use for it. If it is required in the pure state any of the usual processes for making chlorides may be used.

Anhydrous calcium chloride, used as a drying agent, is made by evaporating the solutions and heating to 200° C., or sometimes until the solid product fuses.

*Properties.*—Anhydrous calcium chloride forms white porous masses which fuse at about 775° C. It is exceedingly deliquescent and finds a use as a drying agent for liquids and gases. Since the hydrated salt has a measurable vapour pressure, it is not possible to dry a gas or liquid completely with calcium chloride. *Intensive* drying requires the use of phosphorus pentoxide. Among the gases which cannot be dried with calcium chloride is ammonia, which forms several compounds, such as $CaCl_2.8NH_3$ (*v.* § 694).

Calcium chloride forms several hydrates, the one stable at room temperature being $CaCl_2.6H_2O$. It is extremely soluble in water, 100 gms. of which dissolve 74 gms. at 20° C., and 139 gms. at 60° C. Solutions of very high strength can be prepared which are occasionally used as heating liquids in water-baths. Thus a 325 per cent.

solution of calcium chloride boils at 180° C. Such solutions are much cleaner than oil and safer than sulphuric acid, but it must not be forgotten that they crystallise out on cooling. The hydrate $CaCl_2.6H_2O$ is very soluble and has an extremely low eutectic temperature. Thus the temperature of a mixture of 1·44 parts of the crystallised chloride with 1 part of snow falls to —55° C. The anhydrous chloride cannot be used, as it evolves heat when it becomes hydrated. In its chemical properties calcium chloride resembles other calcium salts and chlorides.

**380. Detection and Estimation of Calcium.**—*Detection.* The flame test for calcium is one of the best, but it is only reliable in absence of the metals, strontium, barium and sodium. The test is applied as follows : The suspected calcium compound is moistened with hydrochloric acid (in order to form the somewhat volatile chloride) and then heated in a Bunsen flame on a platinum wire ; a brick-red coloration is given to the flame. Examined with the spectroscope (a direct-vision pocket instrument does very well), conspicuous lines in the orange and green are noticeable among a large number of others.

Calcium, strontium and barium form a group of elements of which the carbonates are precipitated by ammonium carbonate in presence of ammonia (difference from alkali metals and magnesium), but of which neither the sulphides nor hydroxides can be precipitated in presence of ammonium salts and ammonia (difference from most other metals). The sulphides of these metals are not precipitated from solution because, though insoluble in water, they are hydrolysed to hydrogen sulphide and the hydroxides.

In order to detect calcium in presence of the other two metals it is separated from them by the method describe in § 401.

*Estimation.*—Calcium may be precipitated as oxalate, $CaC_2O_4.H_2O$, by addition of boiling ammonium oxalate solution to a solution containing calcium salts, together with ammonia and ammonium chloride. The precipitate is washed with dilute ammonium oxalate and is best weighed as calcium oxide, after strong ignition. By careful ignition the process may be stopped at the stage of carbonate and the calcium may be weighed as such,

$$CaC_2O_4 = CaCO_3 + CO$$
$$CaCO_3 = CaO + CO_2.$$

Volumetrically, calcium is estimated by precipitation as the oxalate, as described above. The precipitate is washed with water, dissolved in dilute sulphuric acid, heated to 60° C., and titrated with permanganate,

$$5CaC_2O_4 + 8H_2SO_4 + 2KMnO_4 = 5CaSO_4 + K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

This method saves the time needed for drying, igniting and weighing the oxalate.

## STRONTIUM Sr. 87·63

**381. History and Occurrence.**—Strontium was first isolated by Davy in 1808, but the carbonate had been known for some years previously.

*Occurrence.*—Strontium is found as strontium sulphate, *celestine*, so called from the blue colour it often displays. *Strontianite*, strontium carbonate, is also found.

*Preparation.*—The methods described under calcium may be used. The electrolysis of the fused chloride is usually employed.

*Properties.*—It is a white metal of low density. In its chemical properties it resembles calcium but is even more reactive.

*Atomic Weight of Strontium.*—Methods analogous to those used for calcium (§ 355) have been employed and indicate a value of 87·63. Isotopes of masses 86 and 88 are known.

**382. General Properties of Strontium Salts.**—These salts closely resemble those of calcium. They give a brilliant crimson colour to the Bunsen flame with spectral lines in the red, orange and blue.

The precipitation reactions are similar to those of calcium in most respects. Strontium sulphate (*q.v.*) is, however, less soluble than calcium sulphate and is, therefore, more readily precipitated. Strontium chromate, too, is comparatively insoluble.

**383. Strontium Oxide SrO.**—Strontium oxide is made by similar methods to those used for calcium oxide, but higher temperatures are required to decompose the carbonate. Accordingly it is best to heat the nitrate,

$$2Sr(NO_3)_2 = 2SrO + 4NO_2 + O_2.$$

On the commercial scale celestine may be reduced to sulphide by heating with carbon and the sulphide treated with caustic soda,

$$SrSO_4 + 2C = SrS + 2CO_2$$
$$SrS + 2NaOH = Na_2S + Sr(OH)_2.$$

The sodium sulphide is removed by washing with water and the hydroxide is converted into the oxide by heat.

$$Sr(OH)_2 = SrO + H_2O.$$

The oxide much resembles quicklime. It is 'slaked' by water in the same way as the latter, much heat being evolved,

$$SrO + H_2O = Sr(OH)_2 + 19{\cdot}44 \text{ Cal.}$$

*Strontium peroxide* $SrO_2$ has similar properties to calcium peroxide, and is made in the same way; but is also produced by the action of oxygen on heated strontium monoxide.

*Strontium hydroxide* $Sr(OH)_2$ may be made as above or by other methods, including the action of steam on the carbonate at 500–600° C.,

$$SrCO_3 + H_2O = Sr(OH)_2 + CO_2.$$

It resembles slaked lime, but being more soluble in water (0·81 gm. per 100 gms. water at 20° C., 22·7 gms. per 1,000 gms. at 100·2° C.) it displays more powerful alkaline properties.

It finds considerable use in sugar-refining, combining as it does with sugar to form an insoluble compound, which may be filtered off and decomposed by carbon dioxide, thus liberating the sugar.

**384. Salts of Strontium.**—*Strontium carbonate* $SrCO_3$ occurs native as *strontianite*, isomorphous with aragonite. It can be made by the same methods as calcium carbonate. It is, however, technically made in various ways from celestine, which may, for example, be fused with sodium carbonate,

$$Na_2CO_3 + SrSO_4 = Na_2SO_4 + SrCO_3.$$

Strontium carbonate resembles calcium carbonate. It is, however, even less soluble in water. Its solubility, like that of calcium carbonate, is greater in presence of carbon dioxide.

Strontium carbonate is less easily decomposed by heat than calcium carbonate, a temperature greater than 1,200° C. being needed for reasonably rapid decomposition. The preparation of the oxide by heating the carbonate is therefore impracticable under laboratory conditions.

*Strontium nitrate* $Sr(NO_3)_2$ is made by the usual methods, and also on the large scale by the reaction of concentrated strontium chloride and sodium nitrate solutions.

$$SrCl_2 + 2NaNO_3 = Sr(NO_3)_2 + 2NaCl.$$

Strontium nitrate crystallises with four molecules of water of crystallisation, $Sr(NO_3)_2.4H_2O$. It is very soluble in water, 100 gms. of which dissolve 68 gms. of the salt at 20° C.

Strontium nitrate has the usual properties of a nitrate.

It is used in 'red fires' in pyrotechny, the nitrate group supplying the oxygen and the volatilised strontium compounds colouring the flame red.

*Strontium sulphide* SrS is phosphorescent, like calcium sulphide.

*Strontium sulphate* $SrSO_4$ occurs native, as *celestine*. It is easily obtained as a finely crystalline precipitate by the action of sulphuric acid on a solution of a strontium salt.

$$Sr^{++} + SO_4^{--} \rightleftharpoons [Sr][SO_4]$$

Strontium sulphate forms a white powder or transparent crystals very sparingly soluble in water (*c.* 0·01 per cent. at 18° C.). In addition to its smaller solubility the salt differs from calcium sulphate in that it does not form a hydrate.

Strontium sulphate differs also from calcium sulphate in that it is insoluble in a solution of ammonium sulphate. It resembles barium sulphate (*q.v.*) in most of its chemical properties. An *acid sulphate*, $Sr(HSO_4)_2$, is formed when the normal sulphate is dissolved in hot concentrated sulphuric acid and the solution allowed to cool,

$$SrSO_4 + H_2SO_4 = Sr(HSO_4)_2.$$

*Strontium chromate* $SrCrO_4$ is a yellow crystalline powder, sparingly soluble in water (1 : 832 at 15° C.). It is, however, soluble in weak acids, and thereby differs from barium chromate, a fact made use of in qualitative analysis.

*Strontium fluoride* $SrF_2$ is, like the calcium salt, nearly insoluble in water.

*Strontium chloride* $SrCl_2$ is made by the usual methods of preparing soluble chlorides. It resembles calcium chloride in forming a hexahydrate, $SrCl_2.6H_2O$. Like the former salt, it is very soluble in water, 100 gms. of which dissolve 50 of the anhydrous chloride at 18° C. The anhydrous salt is rather less hygroscopic than calcium chloride.

**385. Detection and Estimation of Strontium.**—The flame test, carried out as described in § 380, gives a carmine-red colour, the spectroscope showing a group of lines in the red, orange and blue.

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The detection of strontium in presence of barium and calcium is described in § 401.

Strontium is estimated, either as sulphate like barium (alcohol being added to diminish the solubility), or as carbonate. The volumetric method described under calcium is also available.

## BARIUM Ba, 137·36

**386. History.**—Barium compounds came first into notice when the phosphorescent sulphide was discovered by Casciorolus, a shoemaker of Bologna. In 1774, Scheele distinguished between barium and calcium. The name barium is derived from 'barytes,' the name given to the sulphate on account of its high density (Greek *βαρύς*, *barys*, heavy). The metal was prepared, in 1808, by Davy as an amalgam, but was first prepared in the pure condition by Guntz, in 1901.

**387. Occurrence.**—The commonest barium mineral is the sulphate *barytes* or *heavy spar*. Barium is also found as the carbonate *witherite*, and as the impure barium manganite *psilomelane*.

**388. Preparation.**—Barium is among the most difficult of metals to prepare on account of its great affinity for oxygen. It has been prepared by electrolysis of the chloride with a mercury cathode. The barium dissolves in the mercury and the resulting amalgam is then dried and the mercury distilled off.

The process is difficult on account of the need to remove all traces of water from the amalgam and also on account of the tendency of the barium to retain some mercury even at a high temperature.

Barium oxide can be reduced by means of aluminium powder at 1,200° C.

$$3BaO + 2Al = 3Ba + Al_2O_3.$$

**389. Properties.**—Barium is a fairly soft white metal. It melts at 850° C. and is volatile above 950° C.

Barium is exceedingly reactive, taking fire spontaneously when exposed in powdered form to air.

It decomposes water like calcium, but more vigorously, but differs from that metal in decomposing alcohol.

**390. Atomic Weight of Barium.**—The same methods as those used for the atomic weight of calcium have been employed. The result, 137·37, is the most probable.

**391. Oxides of Barium.**—Three oxides probably exist :—

| | |
|---|---|
| Barium suboxide . . . | $Ba_2O$ |
| Barium oxide . . . . | $BaO$ |
| Barium peroxide . . . | $BaO_2$ |

*Barium suboxide* $Ba_2O$ has been prepared as a blackish mass by heating barium oxide with magnesium.

**392. Barium Oxide BaO** is ordinarily obtained by heating the hydroxide or nitrate to a red heat,

$$Ba(OH)_2 = BaO + H_2O.$$
$$2Ba(NO_3)_2 = 2BaO + 4NO_2 + O_2.$$

The carbonate cannot be decomposed by heat alone but when heated with carbon forms the oxide and carbon monoxide,

$$BaCO_3 + C = BaO + 2CO.$$

At the temperature of the electric furnace carbon will reduce barium sulphate to oxide, the reactions being,

$$BaSO_4 + 4C = BaS + 4CO$$
$$BaS + 3BaSO_4 = 4BaO + 4SO_2.$$

Barium oxide is a white powder, which fuses at a high temperature, lower, however, than the melting-point of lime. It is a basic oxide of the most reactive type. It combines with water with such evolution of heat that under favourable conditions the product may be raised to incandescence.

$$BaO + H_2O = Ba(OH)_2 + 24{\cdot}24 \text{ Cal.}$$

It is an excellent drying agent, especially for organic bases (*e.g.*, pyridine). Carbon dioxide is absorbed with evolution of much heat.

When heated in air barium oxide forms barium peroxide $BaO_2$.

$$2BaO + O_2 \rightleftharpoons 2BaO_2.$$

**393. Barium Peroxide $BaO_2$** is formed by the reversible reaction just mentioned at temperatures above 400° C. The formation of the peroxide evolves heat and is accompanied by a diminution of volume ;

$$2BaO + O_2 \rightleftharpoons 2BaO_2 + 24{\cdot}2 \text{ Cal.}$$

a rise in temperature or a diminution in pressure will cause the barium peroxide to dissociate again more or less completely.

Barium peroxide is a white powder insoluble in water. It forms an octahydrate $BaO_2.8H_2O$.

Heated to redness it decomposes, evolving oxygen. Acids react with barium peroxide, forming hydrogen peroxide (*q.v.*) in the cold and oxygen at higher temperatures. Barium peroxide absorbs carbon dioxide from the air, forming oxygen and barium carbonate.

$$2BaO_2 + 2CO_2 = 2BaCO_3 + O_2.$$

It is an oxidising agent. It finds a commercial use in the manufacture of hydrogen peroxide.

**394. Barium Hydroxide $Ba(OH)_2$.**—The formation from barium

oxide and water has already been mentioned. On the commercial scale various methods are employed. The carbonate may be heated to strong redness in a current of steam, when barium hydroxide and carbon dioxide are formed,

$$BaCO_3 + H_2O \rightleftharpoons Ba(OH)_2 + CO_2.$$

The native carbonate, witherite, may be used, or the carbonate may be made from the sulphate by reducing it at a high temperature with carbon to barium sulphide and treating this with carbon dioxide.

Barium hydroxide is a white powder when anhydrous, but is usually met with as the crystallised octahydrate, $Ba(OH)_2.8H_2O$. When heated the octahydrate melts and loses water. The anhydrous compound melts at 325° C. and begins to decompose at about 600° C., but the action is slow below 900°–1,000° C.

Barium hydroxide is much more soluble in water than calcium or strontium hydroxides. At 15° C. 100 gms. water dissolve 3·23 gms. of anhydrous $Ba(OH)_2$ and about 101 gms. at 100° C. The solution is strongly alkaline owing to its complete dissociation to $Ba^{++}$ and $OH^-$ ions.

Its properties are, therefore, those of an alkali (§ 168), and of a barium salt (§ 395). It finds considerable use in analysis. Barium hydroxide is the only alkali which is reasonably soluble in water and is also always free from carbonate, for any barium carbonate formed by contact with air is precipitated and sinks to the bottom of the vessel. For the accurate titration of weak acids this is a great advantage, allowing as it does a sharp end-point to be attained. The standard solution is usually kept away from air in a piece of apparatus, such as is shown in Fig. 89. The burette may be filled by blowing air into the storage bottle (preferably with bellows or a rubber ball aspirator), all carbon dioxide being excluded by the two soda-lime tubes. Barium hydroxide is also useful for removing sulphuric acid from a solution. If sulphuric acid be exactly neutralised with barium hydroxide the insoluble sulphate can be filtered off, leaving water only behind,

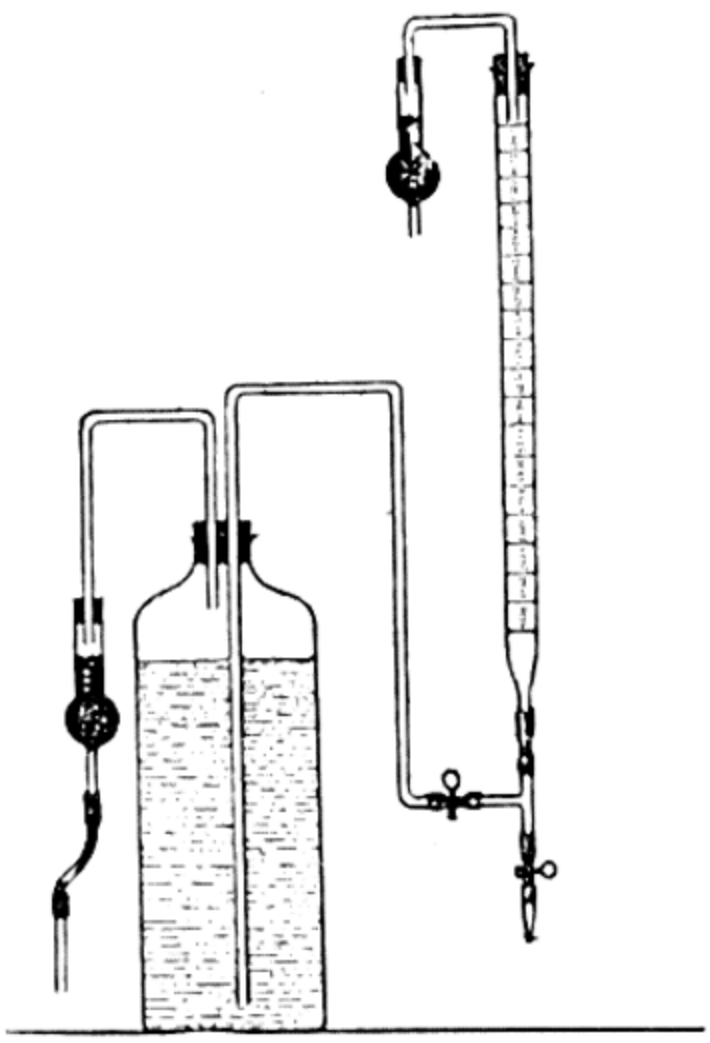

FIG. 89.—Burette for use with baryta solution.

$$Ba(OH)_2 + H_2SO_4 = BaSO_4\downarrow + 2H_2O.$$

**395. General Properties of Barium Salts.**—Barium compounds are in general colourless. They are poisonous to animals and plants. The fatal dose of barium chloride for an adult man is probably about five grams. In the flame test (§ 380) barium salts give an apple-green coloration.

Barium salts in solution give the same precipitates as calcium salts (§ 359), but differ from calcium salts in that they very readily give precipitates with sulphates (§ 399) and also give a lemon-yellow precipitate with solutions of chromates.

$$BaCl_2 + K_2CrO_4 = BaCrO_4 + 2KCl.$$

The ready precipitation of barium sulphate in the cold gives a method for preparing certain unstable acids. Thus permanganic acid (§ 1119) may be made by adding the theoretical quantity of sulphuric acid to a solution of barium permanganate,

$$Ba(MnO_4)_2 + H_2SO_4 = BaSO_4\downarrow + 2HMnO_4.$$

The precipitated barium sulphate settles out and the acid is decanted. This type of preparation gives importance to the preparation of the barium salts of unstable acids.

**396. Barium Carbonate $BaCO_3$** is made by the same methods as calcium carbonate and also, commercially, by reducing the sulphate with carbon to the sulphide and decomposing the latter with carbon dioxide.

$$BaSO_4 + 4C = BaS + 4CO$$
$$BaS + H_2CO_3 = BaCO_3 + H_2S.$$

Barium carbonate is a white powder resembling calcium carbonate in most respects. It is, however, not decomposed at the highest temperature attainable in an ordinary laboratory, decomposition occurring from about 1,200° C. and upwards.

It is very insoluble in water. It dissolves to a small extent in carbon dioxide solution, barium bicarbonate being formed,

$$BaCO_3 + H_2CO_3 \rightleftharpoons Ba(HCO_3)_2.$$

**397. Barium Nitrate $Ba(NO_3)_2$** is made as a rule by double decomposition of sodium nitrate and barium chloride solutions.

It forms colourless anhydrous crystals, moderately soluble in water (100 gms. saturated solution contain 7·7 gms. salt at 18° C. and 25 gms. at 100° C.).

Barium nitrate is one of the least soluble of the nitrates. It is interesting to contrast its low solubility with the great solubility of barium nitrite, of which 100 gms. water dissolve 78 gms. at 18° C. and 461 gms. at 100° C. In its chemical properties it resembles other

nitrates. It finds a use in the preparation of the oxide (§ 392), and also in the making of ' green fire.'

**398. Barium Sulphide BaS** is prepared by reducing the sulphate with carbon,

$$BaSO_4 + 4C = BaS + 4CO.$$

Its properties are similar to those of calcium sulphide, and if traces of certain impurities are present it shines with an orange phosphorescence.

**399. Barium Sulphate $BaSO_4$** is found native as *barytes* or *heavy spar* in crystals, which may be of various colours but which when pure are colourless and transparent. It is the chief source of barium compounds.

In the laboratory it may be made by the action of any soluble barium salt on any soluble sulphate,

$$Ba^{++} + SO_4^{--} \rightleftharpoons BaSO_4.$$

The precipitate is very fine-grained if produced from cold strong solutions, and passes through most filter papers. If boiling solutions are used, and particularly if other salts (*e.g.*, ammonium chloride) are present, there is formed a coarse-grained precipitate, which filters well and settles easily. Very slow precipitation from very dilute solutions produces crystals of visible dimensions.

Barium sulphate is a white solid. It is denser (d. = 4·18) than most salts. It neither melts nor decomposes at temperatures attainable by the Bunsen burner or foot blow-pipe.

The solubility of barium sulphate in water is very low (about 0·000023 per cent at 18° C.), but varies somewhat with the size of the particles, very fine suspensions showing a higher value. It is soluble in concentrated sulphuric acid, forming an acid sulphate, $Ba(HSO_4)_2$, 14·9 gms. dissolving in 100 c.c. of the acid at 25° C.

Barium sulphate is unaffected by heat below 1,500° C. It is unaffected by the action of acids. It is decomposed when heated with carbon, the sulphide (§ 398), or at higher temperatures the oxide (§ 392), being formed.

When fused with an excess of sodium carbonate or boiled with its solution some barium carbonate is formed,

$$BaSO_4 + Na_2CO_3 \rightleftharpoons BaCO_3 + Na_2SO_4.$$

Barium sulphate is used in the manufacture of other barium compounds. It finds uses as a white pigment and is also used as a ' filling ' for mixing with rubber and is also added to paper pulp to give it opacity and weight.

*Barium chromate* $BaCrO_4$ is a lemon-yellow powder, obtained by the action of a solution of a chromate on a soluble salt of barium.

It is insoluble in water and acetic acid and it is thereby distinguished from calcium and strontium chromates.

*Barium fluoride* $BaF_2$, like the calcium salt, is very sparingly soluble in water.

**400. Barium Chloride $BaCl_2$** may be made from the carbonate or hydroxide by the action of hydrochloric acid; but is usually prepared technically from native barium sulphate. A mixture of barium sulphate and coke and calcium chloride is strongly heated,

$$BaSO_4 + CaCl_2 + 4C = BaCl_2 + 4CO + CaS.$$

The mass is extracted with water and to the solution of barium chloride so obtained some lime is added to precipitate any calcium sulphide as the insoluble oxysulphide, CaO.CaS. The barium chloride is crystallised out and recrystallised till pure.

Barium chloride is a white solid when anhydrous, and when crystallised from water forms colourless crystals of formula $BaCl_2.2H_2O$. The anhydrous salt melts at 959° C. Barium chloride is neither hygroscopic nor deliquescent, in these respects differing from the chlorides of strontium and calcium.

Barium chloride is soluble in water. At 20° C. 100 gms. of water dissolve 35·7 gms. of the anhydrous salt and at 100° C. 58·8 gms. In presence of hydrochloric acid or chlorides its solubility is greatly diminished owing to the common ion effect (§ 118). The addition of much concentrated hydrochloric acid to any solution containing a good deal of barium ion therefore causes barium chloride to be precipitated.

Barium chloride has the general properties of barium salts (§ 395), and chlorides (§ 1057). It is not decomposed by heat or hydrolysed by water.

*Barium chlorate* $Ba(ClO_3)_2$ may be made by the action of chlorine on barium hydroxide solution, at 80° C., the chloride being removed by recrystallisation,

$$6Ba(OH)_2 + 6Cl_2 = Ba(ClO_3)_2 + 5BaCl_2 + 6H_2O.$$

It is used for preparing chloric acid (§ 1069), and in the manufacture of 'green fire.'

**401. Detection and Estimation.**—Barium is detected and also estimated by means of the precipitate of barium sulphate instantly formed from even very dilute solutions of barium salts and sulphates.

Barium is detected in presence of calcium and strontium by the following method.

*Detection of Calcium, Strontium and Barium in presence of each other.*—In the qualitative analysis of a mixture which may contain salts of barium, strontium and calcium, the metals, of which the chlorides, hydroxides, or sulphides can be precipitated, are first removed (Pb, Ag, Hg, Cu, Bi, Cd, As,

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Sb, Sn, Fe, Cr, Al, Mn, Co, Ni, Zn). To the solution, made alkaline with ammonia and containing ammonium salts, ammonium carbonate is added when calcium, strontium and barium are precipitated as carbonates if present.

The precipitate is filtered off and examined by one of the usual methods, of which the following, due to Treadwell, is typical.

The precipitate of the carbonates so obtained is dissolved in dilute nitric acid and then evaporated to dryness by cautious heating, expelling the acid and water but not decomposing the nitrates. A part of this residue is dissolved in a little water and calcium sulphate solution is added. If no precipitate appears even on standing, only calcium can be present and its presence is confirmed by the flame test. If a precipitate is formed this must be barium or strontium sulphate and all three metals may be present.

In this event the remainder of the nitrates, which must be dry, is treated with a little absolute alcohol and stirred well. The mixture is filtered. Calcium nitrate is soluble and passes into solution in the alcohol. The filtrate is evaporated to dryness on a watch glass and the residue dissolved in a drop of hydrochloric acid and tested for calcium by the flame test (§ 380).

The residue may contain strontium and barium nitrates. It is mixed with ammonium chloride and heated until no more white fumes are evolved. This converts the nitrates into chlorides,

$$2Sr(NO_3)_2 + 6NH_4Cl = 2SrCl_2 + 5N_2 + Cl_2 + 12H_2O.$$

These chlorides are treated with absolute alcohol as above, and the solution contains strontium chloride, which is detected by evaporation and flame test (§ 385). The residue of barium chloride is washed with alcohol and subjected to flame test (§ 395).

Several other methods are used, based on the different solubilities of the chromates or ferrocyanides.

Barium is estimated gravimetrically by precipitation as sulphate, using the precautions indicated in § 399. The precipitate absorbs traces of other salts present in such a way that they cannot be washed out again. It is therefore advisable in precipitating barium as sulphate to remove other metallic salts as far as possible.

If strontium is present the method cannot be used, since strontium sulphate is also practically insoluble, and it is usual to precipitate the barium as chloride by adding to the solution a large excess of fuming hydrochloric acid and a little ether. Barium chloride is precipitated almost completely and may be filtered off, redissolved in water and precipitated as sulphate.

### RADIUM Ra, 226·05

The preparation and properties of the element are discussed in Chapter XXVI.

# CHAPTER XIII

## ZINC, CADMIUM, MERCURY

**402. Group II. B of the Periodic Table.**—This group of metals shows certain common characteristics. The metals are characterised by low melting point and volatility, these properties becoming more marked as the atomic weights become greater. They each form a series of bivalent salts. Zinc and cadmium compounds show a very close resemblance, but mercury has a chemistry in many respects peculiar. Their relationship to Group II. A in the periodic table and their atomic structure are discussed at the beginning of Chapter XII. It may be noted that while in most groups the elements of greatest atomic weight are the most electropositive, this is not the case with Groups I. B, II. B, or VIII.

### ZINC Zn, 65·38

**403. Historical.**—Zinc was used by the Romans in the form of its ore and its oxide *cadmia*. It was employed in the manufacture of brass, copper ores and calamine being smelted together to yield a copper-zinc alloy. The metal seems to have been accidentally prepared in earlier times, but Kunkel, in 1700, seems to have been the first to recognise it as a separate metal.

**404. Occurrence.**—Zinc is found as—

*Zinc blende*, zinc sulphide. $ZnS$.
*Calamine*, zinc carbonate. $ZnCO_3$.
*Franklinite*, iron, zinc, and manganous oxides.

The first two ores are the most important.

**405. Extraction of Zinc.**—Zinc differs from most metals in that it is volatile enough to be readily distilled, and the principle of the extraction is to convert the ore into oxide and then distil this with carbon in a suitable retort. The carbon reduces the oxide to zinc,

$$ZnO + C = Zn + CO,$$

which distils over and is condensed. Numerous types of process have been evolved, of which the following is typical.

The most important zinc ore is zinc blende. Zinc ore for smelting is required to be fairly concentrated, and it is therefore frequently separated from earthy matter, etc., by the *oil-flotation* process. The finely-crushed ore is mixed with a little oil and then washed with water. The oil adheres to the particles of

metallic sulphide and causes them to float while the earthy matter sinks. The *concentrates* so obtained are then treated in the same way as the massive ore.

If the ore is a sulphide, *e.g.*, zinc blende, it is first roasted. A mechanical roaster is often used and the sulphur dioxide evolved used to make sulphuric acid (§ 929),

$$2ZnS + 3O_2 = 2ZnO + 2SO_2.$$

The zinc oxide so produced is intimately mixed with finely ground coal and heated in a fireclay retort (Fig. 90) to the neck of which is adapted a condenser

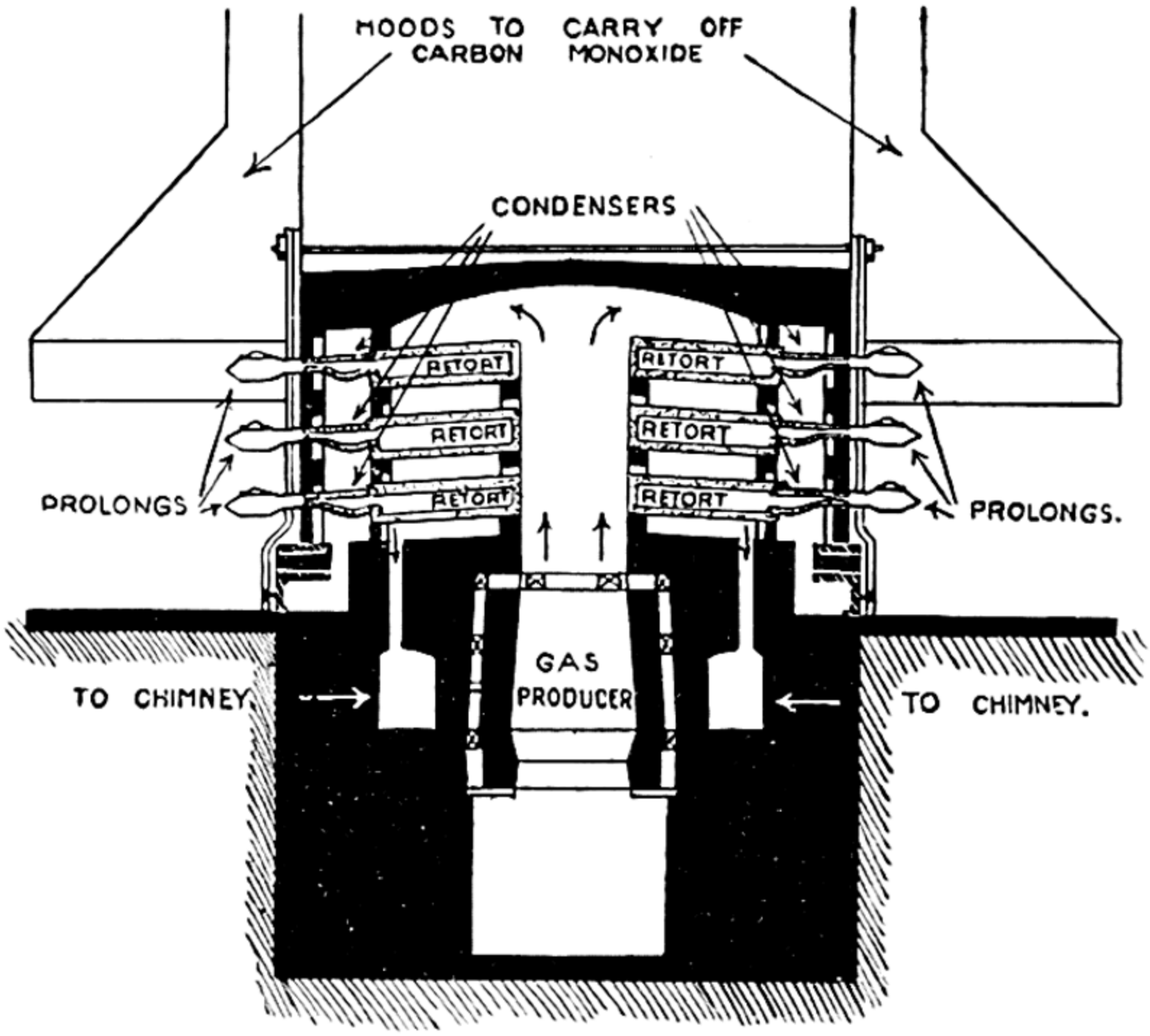


Fig. 90.—Manufacture of zinc in the Rhenish furnace.

of fireclay and a smaller condenser or receptacle, known as a *prolong*. The zinc oxide reacts with the coal, forming zinc and carbon monoxide.

The former condenses partly as liquid metal in the condenser and partly as zinc-dust (mixed with some oxide) in the *prolong*. There are several types of furnace in use but the Rhenish furnace illustrated may be regarded as typical.

Continuously fired retorts, made of silicon carbide, have recently come into use. These are rather more efficient than the older Rhenish furnaces, as conditions throughout the process are uniform and production is continuous.

*Wet Processes.*—Processes based on dissolving the zinc from the ores by means of sulphuric acid (or sodium hydrogen sulphate), and recovering the zinc from the solution by electrolysis, have been used. They yield a very pure zinc, and lend themselves to the recovery of any silver present in the ore. It is estimated that some 20 per cent. of the world's zinc is made in this way, but only where very cheap electricity is available, as in the U.S.A., are they paying propositions.

**406. Properties of Metallic Zinc.**—Zinc is a bluish-white metal

which soon tarnishes to a grey colour. As cast it has a highly crystalline structure and is very brittle. Though brittle below 100° C. and above 200° C., it is malleable and ductile between 100° C. and 150° C. Moreover, sheet zinc, prepared by rolling the hot metal, retains its toughness after it has cooled.

Zinc melts at 420° C. and boils at 930° C. under atmospheric pressure. Its specific heat is 0·092 and its density, which varies with the previous history of the metal, is *c.* 7·1. Zinc is a good conductor of heat and electricity.

*Chemical Properties.*—Zinc burns with a bluish white flame when heated to over 1000° C. Zinc oxide, ZnO, is produced as a smoke and as a bulky mass resembling cotton-wool, formerly called *pompholyx* or ' philosopher's wool.'

Zinc also reacts with chlorine and with sulphur, forming the chloride $ZnCl_2$ and the sulphide ZnS, respectively.

Zinc, if quite pure, is unattacked by boiling water; but commercial zinc, when boiled with water, slowly decomposes it.

Cold water does not attack zinc to an appreciable extent.

Zinc, at a red heat, reacts vigorously with steam, producing zinc oxide and hydrogen.

$$Zn + H_2O = ZnO + H_2.$$

Zinc tarnishes in moist air, becoming covered with a film of oxide, which preserves it from further attack if the atmosphere is not appreciably acid. In large towns zinc is rapidly corroded by the traces of sulphuric acid derived from the burning of coal.

Commercial zinc is readily attacked by all acids, but very pure zinc dissolves only exceedingly slowly. The reason for this is not very certain. An explanation frequently given is that a layer of condensed hydrogen forms on the surface of pure zinc and stops the action of the acid. Impure zinc contains particles of impurity, and these are electronegative to zinc and form with it a number of tiny voltaic cells. Just as in the ordinary voltaic cell the hydrogen is evolved at the *copper* plate, so the hydrogen evolved from impure zinc is evolved from the particles of impurity and leaves the zinc surface free for the acid to attack. In favour of this explanation is the fact that oxidising agents which oxidise the film of hydrogen cause pure zinc to dissolve, and even brushing the surface of the metal brings about the same effect. Thus commercial zinc readily dissolves in dilute sulphuric or hydrochloric acid,

$$Zn + 2HCl = ZnCl_2 + H_2.$$

The reaction is further discussed in § 183.

With nitric acid zinc nitrate is formed. If the acid is concentrated nitrogen peroxide is mainly produced ; if weaker, nitric oxide is the

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chief product ; while dilute nitric acid evolves no gas, being reduced to ammonia which, of course, reacts to form ammonium nitrate.

$$Zn + 4HNO_3 = Zn(NO_3)_2 + 2H_2O + 2NO_2.$$
$$3Zn + 8NHO_3 = 3Zn(NO_3)_2 + 4H_2O + 2NO.$$
$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3.$$

Dilute sulphuric acid gives hydrogen. Hot and stronger acids give hydrogen sulphide, sulphur and, finally, when nearly or quite concentrated, sulphur dioxide together, in each case, with zinc sulphate.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$
$$4Zn + 5H_2SO_4 = 4ZnSO_4 + H_2S + 4H_2O.$$
$$3Zn + 4H_2SO_4 = 3ZnSO_4 + S + 4H_2O.$$
$$Zn + 2H_2SO_4 = ZnSO_4 + SO_2 + 2H_2O.$$

Zinc, in presence of an acid is an excellent reducing agent, the general reaction being

$$Zn + 2HCl + XO = ZnCl_2 + H_2O + X.$$

A mixture of zinc and acid has a reducing power much greater than that of gaseous hydrogen ; the reason of its superior chemical energy is discussed in § 192.

Zinc reacts with hot concentrated solutions of sodium and potassium hydroxides, forming the zincate and hydrogen (cf. § 231).

$$Zn + 2KOH = K_2ZnO_2 + H_2.$$

Zinc reacts with many metallic salts, precipitating the metal, This action is used in the precipitation of gold and silver from the solutions obtained in their extraction by the cyanide process.

**407. Galvanising.**—One of the most important uses of zinc is in the galvanising of iron. Galvanised iron is coated with a thin layer of zinc, which acts as an efficient preservative from rust. This is partly a mechanical protection, the zinc preventing water from reaching the iron, and partly chemical. If a piece of zinc becomes detached, exposing the iron, the metal still will not rust, for the zinc and iron form a galvanic cell, in which the more electropositive metal, zinc, alone dissolves. Thus galvanised iron remains free from rust until all the zinc has disappeared.

Iron articles to be galvanised are first cleaned by 'pickling' them with dilute hydrochloric acid. The acid attacks the iron slightly, loosening the 'scale' or black oxide. The articles are then well washed. The zinc is melted and its surface covered with salammoniac as a flux. The articles are dipped in the molten zinc and withdrawn, covered with a layer of the metal. Wire, wire-netting, sheet iron, etc., are drawn continuously first through the 'pickle' trough and then through the molten zinc.

The electro-deposition of zinc is often preferred to galvanising. The objects to be protected are made the cathode in a bath of zinc sulphate, the anodes being of pure zinc.

**408. Alloys of Zinc.**—The most important of these are brass and die-casting alloys.

Brass consists of copper alloyed with from 20–40 per cent. of zinc. To make it, copper is melted with some flux, such as fluorspar, to protect it from oxidation. Lumps of zinc are then added, a good deal of which burns, producing fumes of zinc oxide.

Brass finds applications in industry on account of its beauty of colour and the ease with which it can be worked by rolling, pressing, spinning, turning in the lathe, etc.

Die-casting alloys are white metals containing zinc, and copper, tin, aluminium, magnesium or nickel, used for precision-casting in metallic moulds.

**409. Atomic Weight of Zinc.**—Dulong and Petit's law, the Periodic law and the vapour density of zinc chloride, zinc ethyl, etc., indicate a value for the atomic weight of about 65.

An exact value has been obtained by similar methods to those employed for magnesium and also by finding the weight of silver displaced from a solution of a silver salt by a given weight of zinc. The value 65·38 is generally adopted.

**410. Zinc Oxides and Hydroxide.**—Zinc oxide has been known for a much longer time than the metal itself. The *cadmia* of the ancients was a deposit in copper smelter's furnaces, and probably consisted of impure zinc oxide. The name *tutia* occurs later and also represents an impure oxide of zinc.

*Pompholyx* was the name anciently given to the zinc oxide evolved as fumes when brass was being made by fusing copper with cadmia (*i.e.*, a zinc ore) and charcoal. The process is mentioned by the ancient author, Dioscorides, 1st cent. A.D. In latter times other names, such as *nix alba*, white snow, were applied to the material.

Zinc oxide is made by the usual methods, including burning the metal and heating the carbonate, both of which are used on the large scale.

Zinc oxide is a white powder, which becomes yellow on heating and loses its colour again on cooling. It is not volatile below a white heat.

The oxide is reduced by carbon at a red heat, as in the manufacture of zinc,

$$ZnO + C = Zn + CO.$$

The oxide is almost insoluble in water (1 : 236,000). It dissolves in acids, giving zinc salts and water, and in alkalis yielding *zincates*,

$$2KOH + ZnO = K_2ZnO_2 + H_2O.$$

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Zinc oxide is used as a pigment, *zinc white*, which has the advantage over white lead of being non-poisonous and unaffected by hydrogen sulphide. Its appearance and covering power is, however, inferior. The oxide is used in medicine in the form of zinc ointment. It is also employed in the manufacture of glazes for certain kinds of porcelain.

*Zinc peroxide* is made by the action of hydrogen peroxide on zinc oxide; the product always contains some monoxide,

$$ZnO + H_2O_2 = ZnO_2 + H_2O.$$

It is a yellowish white powder, which liberates hydrogen peroxide when treated with acids,

$$ZnO_2 + 2HCl = ZnCl_2 + H_2O_2.$$

It finds a use in medicine as a mild antiseptic.

*Zinc hydroxide* $Zn(OH)_2$ is obtained by the action of alkalis on zinc salts,

$$2KOH + ZnCl_2 = Zn(OH)_2 + 2KCl.$$

It decomposes above 100° C. into zinc oxide and water. It behaves as an amphoteric hydroxide, dissolving both in acids to form zinc salts and in alkalis to form zincates.

$$Zn\begin{matrix}OH\\OH\end{matrix} + 2HCl = ZnCl_2 + 2H_2O$$

$$Zn\begin{matrix}OH\\OH\end{matrix} + 2KOH = ZnO_2 . K_2 + 2H_2O$$

$$ZnO_2^{--} + 2H^+ \rightleftharpoons Zn(OH)_2 \rightleftharpoons Zn^{++} + 2OH^-$$

**411. Zincates.**—The zincates are formed by the action of alkalis on zinc (§§ 231, 406) or zinc oxide or hydroxide.

Sodium and potassium zincate are salts of a weak acid and are therefore strongly hydrolysed. Their solutions are strongly alkaline, and when they are diluted with much water and heated, zinc hydroxide is precipitated,

$$Na_2ZnO_2 + 2H_2O = 2NaOH + Zn(OH)_2.$$

In this respect they resemble most salts derived from amphoteric metallic oxides (*e.g.*, aluminates, stannites, plumbites, etc.). The solution of zinc oxide or hydroxide in ammonia does not contain ammonium zincate, but a zinc ammonium complex ion, probably $Zn(NH_3)_4^{++}$ (cf. § 286).

**412. General Properties of Zinc Salts.**—Zinc salts are in general colourless. Most of the salts are very soluble in water. By their dissociation in water they furnish the zinc ion, $Zn^{++}$. Neutral solutions of zinc salts when electrolysed deposit the metal, a somewhat higher voltage being required than is needed for the electrodeposition of most of the metals. Solutions of zinc salts give with alkalis a white precipitate of zinc hydroxide,

$$Zn^{++} + 2OH^- = Zn(OH)_2 \downarrow$$

which dissolves in excess, forming the zincate. With soluble carbonates a precipitate of basic zinc carbonate is precipitated, and with soluble sulphides white zinc sulphide ZnS is precipitated in neutral alkaline or feebly acid solutions.

**413. Zinc Carbonate $ZnCO_3$** occurs native as *calamine*. As prepared by precipitating zinc salts with sodium bicarbonate it has the formula $ZnCO_3$, but if normal sodium carbonate is used the composition of the precipitate is more nearly $ZnCO_3 . 2Zn(OH)_2 . H_2O$.

It is a white powder, readily decomposed by heat, and has been used as a pigment. It is used medically as a lotion for skin diseases, 'calamine lotion.'

**414. Zinc Silicate.**—Zinc orthosilicate $Zn_2SiO_4$ occurs native as *willemite*. The mineral shows a remarkable fluorescence under radio-active radiations or X-rays, and finds a use in the making of X-ray screens.

**415. Zinc Nitrate $Zn(NO_3)_2.6H_2O$** is an exceedingly soluble salt. It has the usual properties of zinc salts and of nitrates.

**416. Zinc Sulphide ZnS** occurs native as zinc blende. It can be made artificially by the action of hydrogen sulphide on an alkaline solution of a zinc salt.

$$Zn^{++} + S^{--} = ZnS.$$

Zinc sulphide is used as a white pigment.

It may be prepared in a phosphorescent form. Pure zinc sulphide is not phosphorescent, but crystalline zinc sulphide containing traces of copper, silver, bismuth, manganese, etc., is luminous. The luminous sulphide may be made by adding 5 gms. sodium chloride and 0·2 to 0·5 gm. of manganese chloride to 20 gms. of pure zinc ammonium sulphate dissolved in 400 c.c. water. The sulphide is precipitated by $H_2S$, filtered off and dried without washing. It is then heated (in a current of hydrogen sulphide) and becomes strongly phosphorescent.

Zinc sulphide not only phosphoresces after exposure to light but also when exposed to X-rays or the $x$-radiation of radium. The luminous paint used on watches is a mixture of zinc sulphide with a radium salt (of which some 0·000001 per cent. is enough to ensure a continuous light).

Zinc sulphide is freely soluble in acids; a zinc salt and hydrogen sulphide being formed,

$$ZnS + 2H^+ = Zn^{++} + H_2S.$$

**417. Zinc Hydrosulphite $ZnS_2O_4$** is readily prepared in solution by the action of zinc on a solution of sulphurous acid,

$$Zn + 2SO_2 = ZnS_2O_4.$$

It should be distinguished from zinc sulphite $Zn(SO_3)_2$. Zinc hydrosulphite is a powerful reducing agent, and is an article of commerce, being used for the decolorising of dyes by reduction.

**418. Zinc Sulphate $ZnSO_4 . 7H_2O$** is sometimes known as white vitriol (*v.* § 938). It is easily made by the action of dilute sulphuric acid on zinc. The salt usually crystallises as $ZnSO_4 . 7H_2O$, but other hydrates exist.

It forms transparent crystals, very soluble in water, 100 gms. of which dissolve 138 gms. of the crystals at 10° C. It finds a use as an emetic in medicine, and as a lotion for the treatment of skin diseases, indolent ulcers, etc.

**419. Zinc Chloride $ZnCl_2$** is obtained by the action of hydrochloric acid on zinc. It is too soluble to be easily crystallised and so is evaporated till the temperature of the liquid reaches 230°–240° C., when the liquid consists of melted zinc chloride, which is poured into airtight drums and allowed to solidify.

The zinc chloride so obtained contains the oxychloride ($ZnCl_2 . nZnO$); the pure anhydrous salt is best made by heating zinc ammonium chloride $3NH_4Cl . ZnCl_2$ in a current of hydrogen chloride.

Zinc chloride forms a white solid which is highly deliquescent. It is poisonous. The solid has caustic properties and is sometimes used in medicine for this purpose. Its solution has been used as a disinfectant. Zinc chloride is exceedingly soluble in water, 100 gms. of water dissolving 330 gms. at 10° C., and at high temperatures it appears to be miscible with water in all proportions.

Zinc chloride has a remarkable power of absorbing water and can be used as a drying agent for gases, etc. Moreover, it has the power, like sulphuric acid, of bringing about reactions in which water is evolved. Thus it is used in organic chemistry as a 'condensing agent.'

Strong zinc chloride solution dissolves cellulose and so cannot be filtered through paper. It also attacks silk, skin and other protein derivatives.

Zinc chloride has all the usual properties of chlorides and of zinc salts.

It combines with zinc oxide to form a hard insoluble zinc oxychloride, and a mixture of these substances is sometimes used as a dental cement. The zinc salts have a preservative action on the pulp of the tooth by destroying bacteria, etc.

Zinc chloride solution is used in soldering as a flux under the name of 'killed spirit' (*i.e.*, hydrochloric acid or spirits of salt neutralised with zinc). It dissolves the coating of oxide on the metal to be soldered.

**420. Detection and Estimation of Zinc.**—There are not many specific tests for zinc. The simplest test for a zinc compound is to heat it with sodium carbonate on charcoal in the blow-pipe flame. Zinc oxide is first formed, which

is reduced to metallic zinc. This is volatilised and re-oxidised, forming on the charcoal an incrustation of zinc oxide which is yellow while hot and white when cold.

In qualitative analysis zinc is usually grouped with cobalt, nickel and manganese. These metals have sulphides which are not precipitated in acid solution, and hydroxides which are not precipitated by ammonia in presence of ammonium chloride. Their sulphides are, however, precipitated by ammonium sulphide (§§ 119, 902). Zinc sulphide is distinguishable from the others of the group by its white colour.

*Estimation of Zinc.*—Zinc is usually determined as zinc ammonium phosphate. A cold acid solution containing the zinc is almost neutralised with ammonia, heated and treated with ammonium phosphate. An amorphous precipitate of

$$Zn^{++} + NH_4^+ + PO_4^{---} = ZnNH_4PO_4,$$

zinc ammonium phosphate comes down and becomes crystalline when heated on the water bath. It is filtered through a Gooch crucible, washed, dried and weighed. The precipitate may also be heated in a crucible and weighed as zinc pyrophosphate (cf. § 350).

$$2ZnNH_4PO_4 = Zn_2P_2O_7 + 2NH_3 + H_2O.$$

A neutral solution of a zinc salt may be titrated with potassium ferrocyanide solution. The reaction is

$$3ZnCl_2 + 2K_4Fe(CN)_6 = 6KCl + K_2Zn_3(Fe(CN)_6)_2.$$

The end point may be detected by adding a little of the solution to spots of ammonium molybdate on a tile. Any excess of ferrocyanide colours this brown.

## CADMIUM Cd, 112·41

**421. Discovery.**—In 1817 a specimen of zinc carbonate was found to be yellowish in colour and in 1818 a specimen of zinc was found to give a sulphide of a yellow colour. K. S. L. Hermann showed that a new element was present. This was named Cadmium after the *cadmia* of the ancients, which was a kind of flue-dust similar to that in which cadmium is found. Stromeyer, in 1817, isolated the metal itself.

**422. Occurrence.**—Cadmium sulphide is found as *Greenockite*. It is, however, chiefly found as a constituent of zinc ores, which commonly contain 0·1 to 0·5 per cent.

**423. Extraction.**—When zinc is distilled from its ores (§ 405) the first portion to distil consists of zinc and cadmium and contains most of the latter metal present in the ore. Further distillations finally bring the cadmium to sufficient purity.

Most of the cadmium recovered is obtained by treating the crude solution of zinc ores in acid, used for the electrolytic manufacture of zinc (§ 405), with zinc dust, which precipitates the less electropositive cadmium.

**424. Properties.**—Cadmium is a white metal. It is fairly hard and not brittle at ordinary temperatures. It melts at 321·7° C. and boils at 778° C. Its density is 8·65.

Cadmium burns readily in air, emitting brown fumes of the oxide. Its reactions are in general closely similar to zinc, though less vigorous.

The metal forms numerous alloys. Copper containing a small proportion of cadmium is coming into use in electrical work. Other alloys of some importance are the fusible metals (*v.* § 829), and cadmium amalgam, which was at one time used for filling teeth and which finds a use in the cadmium standard cell. Cadmium plating is employed for waterproofing piano-wires, certain motor parts and ornamental articles.

**425. Atomic Weight of Cadmium.**—The atomic weight of cadmium has been determined by methods analogous to those used for zinc, and a value of 112·40 is that generally adopted.

**426. Cadmium Oxide CdO** is brown in colour. It is made by the usual methods and is a basic oxide of normal type.

**427. Cadmium Salts.**—The cadmium salts are colourless in solution and are remarkable—in common with mercuric salts—in showing poor conductivity for electricity. This is due to the formation of *auto-complexes*. Thus cadmium chloride ionises to cadmium and chloride ions, $CdCl_2 \rightleftharpoons Cd^{++} + 2Cl^-$, but the ions combine with the undissociated chloride

$$Cd^{++} + 2Cl^- + CdCl_2 = Cd[CdCl_4].$$

Cadmium salts show poor conductivity on account of their very slight dissociation into ions. The most important reaction of cadmium salts is the precipitation of the yellow sulphide, CdS (§ 429).

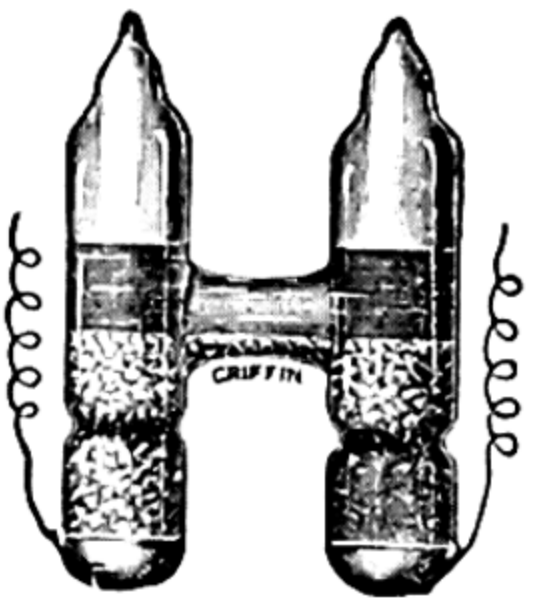


Fig. 91.—Weston Standard Cell.

**428. Cadmium Nitrate . $Cd(NO_3)_2$ . $4H_2O$** is a deliquescent salt, very soluble in water.

**429. Cadmium Sulphide, Cadmium Yellow CdS,** is the most important compound of cadmium. It is prepared by the action of hydrogen sulphide on a solution of a cadmium salt. As the solubility product of cadmium sulphide is not very low, the presence of much acid prevents its precipitation.

The formation of this brilliant yellow sulphide affords a test for cadmium. The only other pure yellow sulphide is that of arsenic. Arsenic sulphide is distinguished from cadmium sulphide by its solubility in ammonium sulphide (*v.* § 804).

Cadmium sulphide, as ordinarily prepared, is a brilliant yellow powder. It exists also in an orange-red form. It finds a use as a pigment for oil and water colours. It must not be mixed with white lead, or the latter will be slowly blackened by formation of lead sulphide.

**430. Cadmium Sulphate $3CdSO_4 . 8H_2O$** is made by the action of sulphuric acid on cadmium oxide. It is used in the Weston Standard Cell, which has the construction shown in Fig. 91. The electrodes are cadmium amalgam and mercury respectively, and the liquid a saturated solution of cadmium and mercurous sulphates. It gives an E.M.F. of 1·019 volts at 15° to 18° C. and the change of E.M.F. with temperature is negligibly small.

**431. Detection of Cadmium.**—The most characteristic reaction of the cadmium ion is its reaction with hydrogen sulphide to form the bright yellow sulphide, CdS. In systematic qualitative analysis it is separated with the metals whose sulphides are precipitated from acid solution. Of these sulphides only those of lead, mercury and bismuth, copper and cadmium are insoluble in ammonium sulphide. From these metals copper and cadmium are readily separated as having hydroxides soluble in ammonia. The detection of cadmium in presence of copper is performed in two ways.

(1) The acid solution of the salts is treated with iron wire. Copper is precipitated, but cadmium, being more electropositive than iron, remains in solution,

$$Cu^{++} + Fe = Fe^{++} + Cu.$$

The solution is filtered and treated with hydrogen sulphide. Ferrous sulphide is not precipitated and the yellow cadmium sulphide indicates the presence of cadmium.

(2) To the solution of the salts potassium cyanide is added until the blue colour of the cupric ion just disappears. Hydrogen sulphide will not precipitate copper but will precipitate cadmium from such a solution. The ions $Cu(CN)_4^{--}$ and $Cd(CN)_4^{--}$ are formed. The former is only very slightly dissociated,

$$Cu(CN)_4^{--} \rightleftharpoons Cu^{++} + 4CN^-,$$

and does not yield enough cupric ion for the solubility product of a cupric sulphide to be reached. The cadmicyanide ion is dissociated to a much greater extent and yields enough $Cd^{++}$ for the precipitation of CdS.

## MERCURY Hg, 200·61

**432. Historical.**—The metal mercury has been known since very early times. It was certainly known to the Romans, who seem to have distinguished between *hydrargyrum*, mercury made artificially, and *argentum vivum*, native mercury. Our name, quicksilver, was derived from the latter. Mercury was at first not regarded as a true metal, and was not given an Alchemical sign, but later it received the sign ☿ of Hermes (Lat. *Mercurius*), the divine patron of the occult sciences. Mercury was one of the chief materials used in alchemy, and until the eighteenth century was regarded as the essential constituent of metals.

**433. Occurrence.**—Mercury occurs occasionally as the native metal, disseminated in globules through the rock, but more commonly as *cinnabar*, mercuric sulphide HgS. This is found chiefly in Spain at Almaden, in Carniola, Tuscany, and in California.

The extraction of mercury from cinnabar-containing ores is accomplished as a rule by heating the ore in a supply of air sufficient to oxidise it to mercury and sulphur dioxide,

$$HgS + O_2 = Hg + SO_2.$$

The mercury is condensed.

Many and various types of furnaces have been used. In the first method the crushed and well-dried ore is fed into a kind of blast furnace, fitted with

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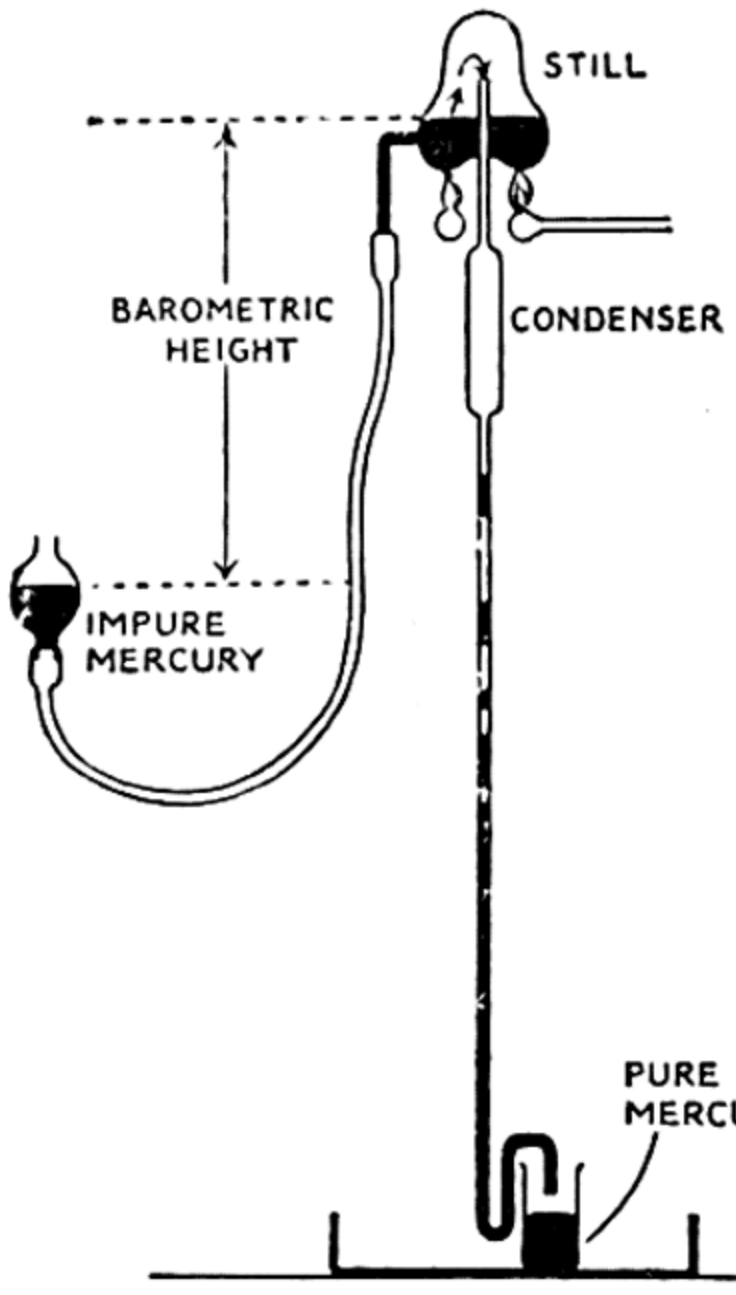


Fig. 92.—Distillation of mercury in vacuo.

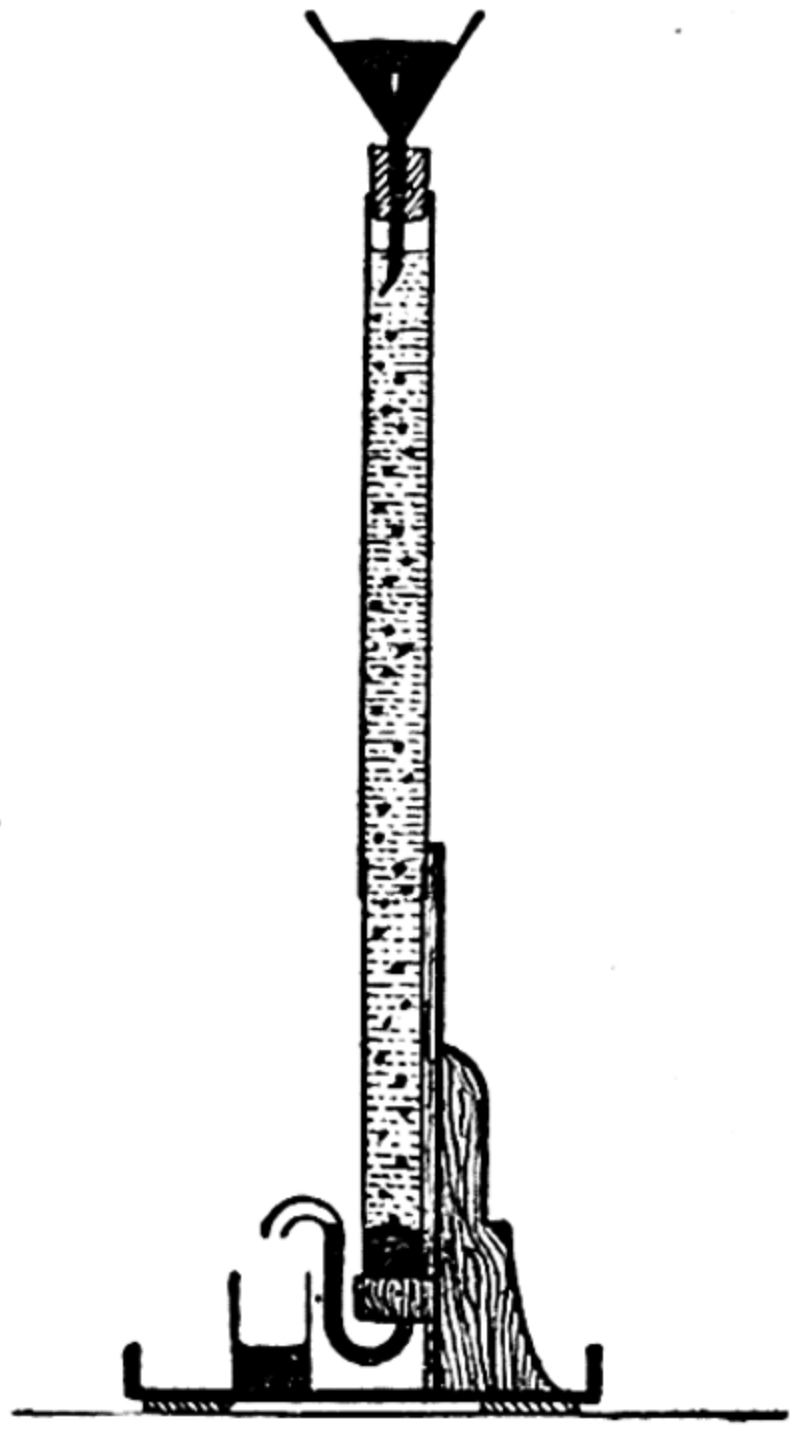

FIG. 93.

sloping shelves, beneath which pass the hot gases from an external fire. The mixture of air, sulphur dioxide and mercury vapour passes through several large chambers, where much of the mercury condenses, the remainder being deposited in long flues.

In other patterns a mixture of ore and charcoal is charged into a small blast furnace, where it burns. The cinnabar is oxidised as above and the gases which leave the furnace are subjected to condensation in brick chambers and flues.

**434. Purification of Mercury.**—The purification of mercury is of importance in laboratory work. The impurities in mercury consist as a rule of baser metals, copper, zinc, etc. Impure mercury is recognised by its ready tarnishing and by the fact that it adheres somewhat to glass so that its globules become pear-shaped when made to run down a sloping glass plate.

The simplest method of purifying mercury from the baser metals is to heat it to 150° C. in a round flask and draw through it a steady stream of air from which dust has been removed by a cotton-wool filter. The impurities oxidise and collect on the surface as a scum, which may be removed by filtration through wash-leather. The process is continued till no more scum is formed.

The simple apparatus of Fig. 94 is also quite efficient. Mercury is placed in the sloping tube and air is drawn through it with a water-pump. The impurities oxidise and collect as a scum which may be filtered off through wash-leather. These processes of oxidation will not remove gold or silver.

Distillation is the only quite satisfactory way of purifying mercury, but the 'bumping' is so violent under laboratory conditions that the process is almost impracticable.

By distillation under highly reduced pressure it is, however, easy to obtain very pure mercury. An ingenious piece of apparatus has been devised by which mercury is heated and the condensed droplets operate a Sprengel vacuum pump and maintain the vacuum. Such an apparatus is shown in Fig. 92.

If this apparatus is not available advantage may be taken of the fact that a dilute solution of mercurous nitrate will react with all base metals forming their nitrates and mercury. Even silver reacts to some extent.[1] The mercury is allowed to flow in a stream of fine droplets through a solution of nitric acid (*e.g.*, 1·1). Some mercurous nitrate is formed and reacts with the base metals present. If much impurity is present the process will need frequent repetition. The apparatus shown in Fig. 93 may be used.

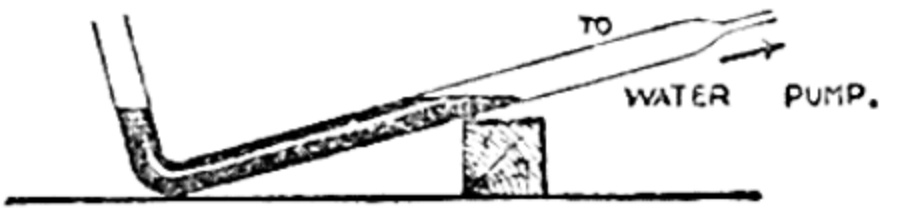


FIG. 94.

**435. Physical Properties of Mercury.**—Mercury is the only metal permanently liquid at the ordinary temperature (but *v.* § 519). It has a brilliant silver-like lustre. Mercury solidifies at —38·85° C. to a white lustrous metal. It boils at 357° C., at 760 mm., forming a monatomic vapour. It is volatile even at ordinary temperatures, and its vapour is poisonous to those exposed to it for long periods. Mercury has a density of 13·546 gms./cm.$^3$ at 20° C. For a metal, it is a poor conductor of heat and electricity, having an electrical conductivity less than a fiftieth of that of silver.

Mercury has a powerful action on the bodily functions. If the vapour is inhaled or if the metal is rubbed into the skin in the form of an ointment it has a strong curative action on certain serious diseases. The prolonged inhalation of the vapour or the taking of an excessive quantity of mercurial medicines finally produces serious illness, causing a copious flow of saliva, loosening of the teeth, and finally death.

For medical purposes metallic mercury is occasionally still used in the form of the 'blue pill,' made by grinding mercury, liquorice, chalk, etc., to a grey mass. The action of this is probably due to traces of oxide. For many purposes mercury is rubbed with grease or oil until it is *deadened* or converted into globules so fine that a powerful microscope is needed to see them. The ointment is rubbed into the skin or the oil injected into the muscles.

**436. Chemical Properties of Mercury.**—Mercury is slowly oxidised when heated in air or oxygen to a temperature of about 350° C., the red oxide being formed,

$$2Hg + O_2 = 2HgO.$$

[1] The reaction, $Hg + AgNO_3 \rightleftharpoons HgNO_3 + Ag$, is an equilibrium reaction, and if mercurous nitrate is present in great excess, silver goes into solution.



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It reacts vigorously with chlorine, forming mercuric chloride,

$$Hg + Cl_2 = HgCl_2.$$

Mercury reacts directly with sulphur and iodine when rubbed with the solids in a mortar.

Most dilute acids have no effect, but dilute and concentrated nitric acid and hot concentrated sulphuric acid attack it. Nitric acid, if dilute, forms mercurous nitrate; if concentrated, mercuric nitrate. Hot concentrated sulphuric acid reacts with mercury, forming sulphur dioxide, and if there is an excess of acid, mercuric sulphate; if an excess of mercury is present mercurous sulphate is produced. It is attacked by hydriodic acid on account of the formation of the $HgI_4^{--}$ ion (§ 278).

Mercury is not affected by water or alkalis.

**437. Amalgams.**—Mercury dissolves nearly all the metals and forms what are called amalgams. These are, as a rule, a solution in mercury of a compound of the metal and mercury. If much mercury is present they form soft bright buttery masses, but may also be hard and metallic in appearance and consistency.

*Sodium amalgam* is made by dissolving clean sodium in mercury. The sodium dissolves with a bright flash and forms the solid compound, NaHg. Sodium amalgam is a useful reducing agent, evolving hydrogen in presence of water.

The so-called *Ammonium amalgam* is made by the action of sodium amalgam on ammonium chloride. It forms a peculiar buttery porous mass which soon decomposes into mercury, ammonia and hydrogen. Whether it contains free ammonium $NH_4$ is at least doubtful.

*Tin amalgam* was at one time used for the 'silvering' of mirrors.

*Copper amalgam* has the useful property of softening when heated to 100° C. and setting hard within a few hours.

Amalgams are made by various methods. The simplest is to mix mercury and the liquid metal, or to rub the metal, preferably in filings, in a mortar with mercury. A method which is available for metals like iron, which do not easily amalgamate, is to place some zinc or sodium amalgam in a solution of the metal. The sodium goes into solution, displacing the metal from its salt. The metal, in its freshly precipitated state, easily dissolves in the mercury.

$$2Na + FeSO_4 = Na_2SO_4 + Fe.$$

Again, the finely divided metal may be covered with a solution of mercuric chloride or nitrate. It displaces the mercury from combination and the deposited mercury amalgamates with the residue of metal. Thus copper is amalgamated by placing it in mercuric nitrate solution.

**438. Uses of Mercury.**—Its great density, its opacity, its slight volatility, its electrical conductivity, and the fact that it does not wet glass, makes mercury invaluable in the construction of physical apparatus. It finds other uses in the manufacture of vermilion and

in the extraction of gold and silver from their ores. A certain amount is used in medicine.

**439. Atomic Weight of Mercury.**—Dulong and Petit's law, the vapour density of volatile mercury compounds and its position in the periodic table indicate an approximate atomic weight of 200. The exact atomic weight has been best determined (1) electrochemically (cf. p. 296); (2) by converting the chlorides of mercury into silver chloride. These methods indicate a value of 200·61. Mercury consists of at least six isotopes of atomic weights, 202, 200, 199, 198, 201, 204, 196.

Bronsted and Hevesey effected a partial separation of these by allowing mercury to evaporate at a low pressure. The heaviest atoms are ejected with the least rapidity and they were able in this way to obtain two specimens of mercury differing in density to the extent of 0·05 per cent. The atomic weight of the two samples differed in the same proportion, *e.g.*, by about 0·1.

**440. Mercurous and Mercuric Compounds.**—Mercury forms two series of compounds, the *mercuric* compounds in which the metal is divalent, and the mercurous compounds which contain the divalent group $Hg_2$, and in which the metal is effectively monovalent.

Thus we have:

| Mercuric Compounds. | Mercurous Compounds. |
|---|---|
| $HgO$ | $Hg_2O$ |
| $HgCl_2$ | $Hg_2Cl_2$ |
| $HgSO_4$ | $Hg_2SO_4$ |
| $Hg(NO_3)_2$ | $Hg_2(NO_3)_2$ |

The mercuric compounds in solution yield the ion $Hg^{++}$, though not to any great extent, for their solutions are much less dissociated than corresponding solutions of other metals.

The mercurous compounds yield the ion $Hg_2^{++}$, *not* $Hg^{+}$.

**441. Oxides of Mercury.**—These are probably only two:—

| | |
|---|---|
| Mercuric oxide . . . . | $HgO$ |
| (Mercury peroxide . . . . | $HgO_2$) |

The black so-called *mercurous oxide* is obtained by the action of an alkali on a mercurous salt. Its X-ray diagram is of the pattern to be expected from a mixture of mercuric oxide and mercury,

$$Hg_2(NO_3)_2 + 2KOH = Hg + HgO + H_2O + 2KNO_3.$$

It is a black powder from which gentle heat separates mercuric oxide and mercury.

It combines directly with oxygen above 100° C., forming mercuric oxide.

**442. Mercuric Oxide HgO.**—This oxide is produced when mercury is heated in air at about 350° C., but is usually made by the reaction of boiling solutions of potassium carbonate and mercuric chloride. The precipitate formed is boiled for some time. Since mercuric

carbonate is not stable the oxide is formed,

$$HgCl_2 + K_2CO_3 = HgO + CO_2 + 2KCl.$$

The *red* variety of the oxide is produced in this way. There is also a *yellow* variety which is less stable and more reactive. The only difference appears to be that of particle size ; small particles have more surface energy per unit weight of material and are therefore more soluble, less stable and more reactive. It is prepared by the action of alkalis on mercuric salts in the cold,

$$HgCl_2 + 2KOH = HgO + H_2O + 2KCl.$$

The red form of mercuric oxide is a bright red crystalline powder, which darkens when heated and regains its colour when cooled. It is nearly insoluble in water. Mercuric oxide is, like most mercuric compounds, highly poisonous.

It is a comparatively unstable substance. When heated it decomposes below a red heat into mercury and oxygen (§§ 856, 860).

$$2HgO = 2Hg + O_2.$$

This reaction is of interest as being that by which oxygen was first prepared.

In addition to the usual properties of a basic oxide, mercuric oxide is a strong oxidising agent. Mixtures of the oxide with sulphur or phosphorus explode violently when heated.

**443. The Mercuric Salts.**—The solutions of the soluble mercuric salts (the chloride, sulphate and nitrate) have certain reactions in common, which may be attributed to the mercuric ion, $Hg^{++}$, which is present in their solutions, though not in any large proportion.

Solutions of mercuric salts are colourless, have a powerful metallic taste and are very poisonous.

They give precipitates of insoluble mercuric salts with many reagents.

The caustic alkalis give a yellow precipitate of mercuric oxide,

$$Hg^{++} + 2OH^- = HgO + H_2O.$$

Ammonia forms white basic salts (cf. p. 380). Hydrogen sulphide gives a black precipitate of mercuric sulphide HgS, which is insoluble in dilute nitric acid (2–3 N), differing thereby from all other precipitated sulphides.

Potassium iodide precipitates the brilliant orange-scarlet mercuric iodide, which redissolves in excess of the reagent, forming

$$Hg^{++} + 2I^- = HgI_2$$
$$HgI_2 + 2I^- = HgI_4^{--},$$

potassium mercuri-iodide which, mixed with potassium hydroxide,

constitutes Nessler's solution (*v.* § 456), used as a reagent for detecting small traces of ammonia.

Reducing agents convert mercuric salts into the mercurous salts (*v.* under mercuric chloride, § 455) and finally into metallic mercury. When electrolysed mercury is produced. The metal is displaced from its salts by all others except the platinum metals and gold, as described in the succeeding section.

The above reactions are given by all soluble mercuric salts, except the cyanide, which is hardly at all dissociated and yields only traces of the mercuric ion.

Mercuric salts are ionised to a much smaller extent than any others. The dissociation constant of mercuric chloride is about $10^{-14}$, while that of an ordinary salt is more than unity, and in most cases infinite. Accordingly, solutions of mercuric salts are very poor conductors. Other consequences follow. Thus, owing to the minute concentration of chloride ion, sulphuric acid liberates no hydrogen chloride from mercuric chloride ; for the amount of hydrogen chloride formed by the reaction $H^+ + Cl^- \rightleftharpoons HCl$ never exceeds its solubility in the acid.

Mercuric chloride solution dissolves silver chloride. The amount of chloride ion from the silver chloride, small as it is, is far more than can be in equilibrium with the mercuric chloride, and the solubility product of the silver chloride is not attained.

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$
Solid
$$Cl^- + HgCl^+ \rightleftharpoons HgCl_2.$$

Finally, most surprisingly, if yellow mercuric oxide is shaken with potassium chloride quite a considerable amount of caustic potash is formed in consequence of the reactions.

$$(a)\ HgO + H_2O \rightleftharpoons Hg^{++} + 2OH^-$$
$$(b)\ Hg^{++} + 2Cl^- \rightleftharpoons HgCl_2.$$

The mercuric ion formed in equilibrium (*a*) is much more than can remain in equilibrium in (*b*). Hence mercuric oxide goes into solution and $OH^-$ ion accumulates.

**444. Mercurous Salts.**—The mercurous salts are for the most part insoluble in water and the nitrate is the only common soluble compound.

Mercurous salts contain the double ion, $^+(Hg-Hg)^+$, for the vapour density of mercurous chloride corresponds to the double formula $Hg_2Cl_2$, and molecular weight determinations based on the depression of the freezing point of solutions indicate the same multiplicity. Moreover the vibrations of the Hg – Hg bond in the mercurous ion have been detected spectroscopically.

Mercurous salts give a black or dark brown precipitate with alkalis,

$$Hg_2(NO_3)_2 + 2KOH = Hg + HgO + 2KNO_3 + H_2O.$$

With hydrogen sulphide a black precipitate is formed, containing mercuric sulphide and mercury.

Potassium iodide precipitates green mercurous iodide $Hg_2I_2$, which immediately breaks up into mercury and mercuric iodide. The action of all metals, except gold and the platinum metals, upon soluble mercury salts is to displace the mercury from combination. The mercury so formed amalgamates with the remainder of the metal (§ 437).

**445. Carbonates of Mercury.**—These salts are unstable. Mercurous carbonate $Hg_2CO_3$ decomposes, forming mercuric oxide, mercury and carbon dioxide at 100–130° C. Normal mercuric carbonate does not exist, but some ill-defined basic salts are known.

**446. Mercuric Cyanide $Hg(CN)_2$** is of interest as being a metallic salt, which is hardly ionised at all in aqueous solution. When heated it evolves cyanogen (§ 573).

**447. Mercury Fulminate $2Hg(CNO)_2.H_2O$** is of value as an explosive. It is prepared by adding alcohol to a solution of mercury dissolved in an excess of nitric acid. The preparation should not be undertaken by the student, for the explosion of this compound is likely to cause serious injury.

Mercuric fulminate is an explosive of great violence. It explodes very suddenly when struck or heated, and produces a violent shock which is of such a character as to cause other more stable substances, such as picric acid $C_6H_2(NO_2)_3OH$, to explode. It is therefore employed in the detonators used in blasting and in warfare to cause the explosion of dynamite, picric acid, etc.

**448. Mercuric Thiocyanate $Hg(CNS)_2$** forms a white precipitate when an excess of mercuric chloride is added to sodium thiocyanate solution. When ignited it forms a voluminous ash, and the so-called *Pharaoh's serpents* are pellets of mercuric thiocyanate made up with gum. When ignited they burn, forming a curious worm-like structure of ash, etc.

**449. Mercurous Nitrate $Hg_2(NO_3)_2 . 2H_2O$** is the only soluble mercurous salt. It is prepared by the action of warm dilute nitric acid (sp. gr. 1·2) upon an excess of mercury. When no further reaction occurs the liquid is decanted from the excess of mercury and left to cool and crystallise.

Mercurous nitrate is a white crystalline salt. It is soluble in water containing nitric acid, but with pure water forms a basic nitrate. In order, therefore, to prepare a solution of the normal salt it must be dissolved in dilute nitric acid.

Mercurous nitrate is decomposed on heating into mercuric oxide and nitrogen peroxide,

$$Hg_2(NO_3)_2 = 2HgO + 2NO_2.$$

Its solution gives, with chlorides, a white precipitate of mercurous chloride, and it shows the precipitation reactions described under mercurous salts (§ 444).

**450. Mercuric Nitrate $Hg(NO_3)_2 . 2H_2O$** is obtained by heating mercury or mercurous nitrate with nitric acid until no precipitate of

calomel is given by a test portion to which a solution of a chloride has been added.

It has the usual reactions of a mercuric salt and of a nitrate. It reacts with water to form a white insoluble basic nitrate,

$$2Hg(NO_3)_2 . 2HgO,$$

and it must therefore be dissolved in dilute nitric acid.

**451. Mercuric Sulphide, Vermilion, Cinnabar, HgS.**—Mercuric sulphide is found native as a red mineral, cinnabar, which is the chief source of mercury (§ 433).

Cinnabar is not pure enough for use as a pigment, and mercuric sulphide is therefore prepared artificially.

Mercuric sulphide exists as (*a*) a black amorphous variety ; (*b*) a red crystalline variety.

(*a*) The black sulphide is made by rubbing mercury and sulphur together in a mortar or by passing hydrogen sulphide through a solution of a mercuric salt, usually the chloride

$$HgCl_2 + H_2S = 2HCl + HgS.$$

The precipitate is at first whitish, then changes to yellow-brown and finally black. The intermediate stages are compounds or mixtures of the sulphide and chloride.

(*b*) The red variety, which forms the valuable pigment vermilion, is made by preparing the black sulphide and then subliming it, when it condenses as the red variety.

Mercuric sulphide is a black or brilliant red solid, insoluble in water, and hardly attacked by acids.

When heated, it decomposes into mercury and sulphur, and if air is present the latter is oxidised to the dioxide,

$$HgS + O_2 = Hg + SO_2.$$

It is reduced to metal by heating with sodium carbonate, lime, iron filings, etc. (§ 433). The red form is attacked by boiling nitric acid and forms a white insoluble compound. The black form dissolves in moderately dilute nitric acid, forming mercuric nitrate.

Aqua regia attacks it.

$$HgS + Cl_2 = HgCl_2 + S.$$

It is soluble in sodium sulphide solution, forming a complex salt.

Mercuric sulphide finds considerable use as a pigment. It has a very beautiful colour and is extremely permanent. Vermilion lettering in illuminated manuscripts a thousand years old retains all its brilliance of colour. Its cost precludes its use for large scale

decoration, and red lead, which is far less permanent, is ordinarily used.

*Mercurous sulphide* does not exist (§ 444).

**452. Mercurous Sulphate $Hg_2SO_4$** is prepared by the action of sulphuric acid on mercury at the lowest temperature at which the action will take place,

$$2Hg + 2H_2SO_4 = Hg_2SO_4 + 2H_2O + SO_2,$$

or by adding sulphuric acid to mercurous nitrate solution,

$$Hg_2^{++} + SO_4^{--} \rightarrow Hg_2SO_4 \downarrow$$

It is a white solid, almost insoluble in water. It finds a use in the Weston Standard cell (§ 430).

**453. Mercuric Sulphate, $HgSO_4$** is prepared by heating mercury strongly with an excess of sulphuric acid and evaporating, when small silvery crystals are produced on cooling,

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2.$$

Mercuric sulphate forms small white crystals soluble in water. When heated strongly mercurous sulphate, mercury, sulphur dioxide and oxygen are formed.

It dissolves in cold water but reacts with hot water to form the red basic sulphate, 'turpeth mineral,'

$$3HgSO_4 + 2H_2O = HgSO_4 . 2HgO + 2H_2SO_4.$$

**454. Mercurous Chloride, Calomel, $Hg_2Cl_2$.**—Mercurous chloride has been known since the early Middle Ages, and the Chinese and Japanese have prepared it and used it medicinally for many centuries. The name is probably derived from the Greek καλός, beautiful, and μέλας, black. The reason of the application of the word 'black' to this white salt is doubtful. Among various suggestions we may note the fact that it was a remedy for '*black* bile' (melancholia) and also that it is blackened by alkalis.

Calomel is prepared by grinding mercuric chloride with mercury till the latter is 'deadened' or converted into a grey mass of invisibly small globules, and subliming the product,

$$HgCl_2 + Hg = Hg_2Cl_2.$$

The solid cake of sublimate is ground and washed with boiling water till no trace of the very poisonous mercuric chloride remains.

This salt is also made by converting mercury into mercuric sulphate, grinding this thoroughly with common salt and metallic mercury and subliming the mass and purifying it,

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$$

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4$$
$$HgCl_2 + Hg = Hg_2Cl_2,$$

as above.

In the laboratory the simplest method is to heat 9 parts of mercury with 8 parts of nitric acid (sp. gr. 1·2) until no more can be dissolved, mercurous nitrate being formed,

$$6Hg + 8HNO_3 = 3Hg_2(NO_3)_2 + 4H_2O + 2NO.$$

To this is added a boiling solution of common salt acidified with a little hydrochloric acid. Insoluble mercurous chloride is precipitated, filtered off and repeatedly washed to remove any traces of mercuric chloride,

$$Hg_2(NO_3)_2 + 2NaCl \rightleftharpoons Hg_2Cl_2 + 2NaNO_3.$$

*Properties.*—Mercurous chloride is a white powder, without taste or smell and insoluble in water. It acts as a purgative and cholagogue, and finds considerable use in medicine. For this purpose it must be free from mercuric chloride. The presence of this impurity is best detected by mixing the solid with water and immersing a clean knife blade, on which a black stain of mercury will be produced if as little as 0·00002 gm. of mercuric chloride is present.

Calomel vaporises when heated and the vapour consists of a mixture of mercury and mercuric chloride vapour,

$$Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2.$$

Its vapour density therefore corresponds to the value for the formula HgCl. The lowering of the freezing point (§ 60) of fused mercuric chloride by calomel also indicates this formula.

In addition to the usual reactions of mercurous compounds calomel forms a remarkable black compound with ammonia. This consists of a mixture of mercuric aminochloride and mercury.

$$Hg_2Cl_2 + 2NH_3 = Hg + Hg\begin{<}{Cl}{NH_2}\end{} + NH_4Cl,$$

Calomel may possibly be named from the production of this compound. Mercuric chloride (*v. infra*) forms only the white mercuric aminochloride under these conditions,

$$HgCl_2 + 2NH_3 = HgClNH_2 + NH_4Cl.$$

**455. Mercuric Chloride, Corrosive Sublimate, $HgCl_2$.**—Mercury is readily converted into this salt by the action of chlorine or of aqua regia.

$$Hg + Cl_2 = HgCl_2.$$

On the large scale mercuric sulphate is made by heating mercury for a long time with a slight excess of sulphuric acid and evaporating to dryness. The mercuric sulphate is mixed with common salt

and a little manganese dioxide and sublimed onto the lids of iron pots.

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$$
$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

Mercuric chloride forms white crystalline lumps, soluble in water (100 gms. dissolve 5·6 gms. at 10° C., 56 at 100° C.) and in alcohol. It has a strong metallic taste and is intensely poisonous. The best antidote is albumen—*raw* white of egg, with which it forms an insoluble precipitate. Sodium thiosulphate—'hypo'—is also a remedy, probably forming the insoluble sulphide HgS. Its power of destroying bacteria makes mercuric chloride a most efficient disinfectant and antiseptic, a weak solution (1 : 1,000) being used as a disinfectant in surgical practice and for dressing wounds.

Mercuric chloride vaporises at comparatively low temperature. It melts at 288° C. and boils at 303° C.

Mercuric chloride is only slightly dissociated in solution and its solutions are therefore poor conductors of electricity (§ 443).

In solution mercuric chloride slowly decomposes, giving calomel. This reaction, as also its reaction with certain reducing agents, such as oxalates, occurs only in the light, and a photometer has been constructed depending on this reaction.

Reducing agents, when added to mercuric chloride solution, produce a white precipitate of calomel. The reduction may proceed further and produce metallic mercury. Stannous salts, arsenites, oxalic acid, etc., bring about these reductions:

$$Sn^{++} + 2Hg^{++} = Sn^{++++} + Hg_2^{++}$$
$$Sn^{++} + Hg_2^{++} = Sn^{++++} + 2Hg.$$
$$2HgCl_2 + C_2H_2O_4 = 2CO_2 + Hg_2Cl_2 + 2HCl.$$

Mercuric chloride forms a compound with ammonia, $NH_2 . HgCl$, which is known as mercuric aminochloride or mercuric chloroamide, also as *infusible white precipitate*.

$$HgCl_2 + NH_3 = NH_2 . HgCl + HCl.$$

It is a white powder which volatilises below its melting-point. A very large number of amino-halogen mercury compounds exists. The compound formed by the ammonia on Nessler's solution (*v.* mercuric iodide) is one of these.

**456. Mercuric Iodide $HgI_2$** is prepared by the action of potassium iodide on mercuric chloride, avoiding an excess of the former,

$$Hg^{++} + 2I^- \rightleftharpoons HgI_2. \downarrow$$

The precipitate is at first a beautiful salmon-pink, but later becomes a fine and brilliant scarlet.

Mercuric iodide exists in two forms, a red variety, stable below 126°, and a yellow form, stable above this temperature. If the yellow variety is prepared by heating the red variety and is then changes to cool, it remains yellow until touched, when it instantly allowed to the red modification.

Mercuric iodide dissolves in potassium iodide solution to form a solution from which potassium mercuric iodide $K_2HgI_4$ can be crystallised. An alkaline solution of the latter salt is known as Nessler's solution and is distinguished by giving a yellow coloration or brown precipitate with the smallest traces of ammonia. This precipitate is oxydimercuriammonium iodide $(OHg_2)NH_2I$.

The solution of mercuric iodide in potassium iodide is employed in medicine as an antiseptic. It is more efficient than mercuric chloride and does not attack metal with deposition of mercury as does the former.

**457. Detection and Estimation of Mercury.**—The best tests for mercury depend on the separation of the metal. Thus, if a piece of copper foil is boiled with a solution of a mercury salt, a layer of mercury, which becomes bright and silvery when rubbed, is deposited on it. Gentle heating in a bulb-tube volatilises the mercury, which condenses on the walls of the tube as a sublimate of bright globules.

All mercury compounds, when heated with anhydrous sodium carbonate, yield the metal, and the heating of a mixture of an excess of the latter salt with a suspected substance, affords a good test for mercury,

$$2HgS + 2Na_2CO_3 = 2Na_2S + 2Hg + 2CO_2 + O_2.$$

Lime and iron filings both have a similar effect,

$$2Hg_2Cl_2 + 2CaO = 2CaCl_2 + 4Hg + O_2$$
$$Fe + HgSO_4 = FeSO_4 + Hg.$$

*Estimation.*—The last process may be employed to estimate mercury by performing it in a crucible covered with a water-cooled and weighed silver plate. The mercury condenses upon the plate and its weight is thus determined.

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# CHAPTER XIV

## BORON, ALUMINIUM AND THE METALS OF GROUP III.

**458. Group III. of the Periodic Table.**—Group III. of the Periodic table contains only two common elements, Boron and Aluminium. The complete group is now usually classified as below :—

| III. A. | III. B. |
|---|---|
| | Boron. |
| | Aluminium. |
| Scandium. | |
| | Gallium. |
| Yttrium. | |
| | Indium. |
| Lanthanum. | |
| [Rare Earths.] | Thallium. |
| Actinium. | |

The question of whether boron and aluminium are to be classified with scandiun, yttrium, lanthanum and actinium, or, on the other hand, with gallium, indium and thallium, has occasioned some difficulty. The most recent work indicates the above arrangement as the best.

Scandium, yttrium and lanthanum can be shown on the grounds of spectra, etc., to have affinities to the transition elements. None the less a good case, on *chemical* grounds, could be made out for classifying gallium, etc., as transition elements and scandium, yttrium and lanthanum as normal elements.

The conclusion has been reached that the elements boron, aluminium, gallium, indium, thallium have a structure characterised by the possession of three valency electrons in the outermost quantum group.

| Atomic Number. | Element. | Electrons with quantum-number | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| 5 | Boron . | 2 | 3 | | | | |
| 13 | Aluminium . | 2 | 8 | 3 | | | |
| 31 | Gallium . | 2 | 8 | 18 | 3 | | |
| 49 | Indium . | 2 | 8 | 18 | 18 | 3 | |
| 81 | Thallium . | 2 | 8 | 18 | 32 | 18 | 3 |

A similar table for Group III. A is given in § 504a.

The elements of this group, boron and aluminium excluded, are all so rare that a general discussion of their properties is unnecessary. In general, it may be stated that the elements of the group are all tervalent (Group III. B shows lower valencies also), and with the exception of boron all are metals.

## BORON B, 10·82

**459. History.**—Borax was probably not known before the eighth century A.D., though the Greek word, 'Chrysocolla,' used in much earlier times, has sometimes been so translated.

The element was discovered in 1808, being prepared by Gay-Lussac and Thènard, who heated boric oxide with potassium.

**460. Occurrence.**—The element does not occur free but only as *boric acid* (*q.v.*), and as *borates* including *kernite*, sodium tetraborate $Na_2B_4O_7 . 4H_2O$, *boracite*, *colemanite* and *pricite*, all calcium borates; *ulexite*, a double borate of sodium and calcium; and as a few rare minerals.

**461. Preparation.**—There were formerly considered to be two allotropic forms of boron, the amorphous and the crystalline.

It is however now clear that these are, or contain, compounds with aluminium, carbon, or magnesium.

The so-called amorphous boron is best prepared from the oxide by the action of magnesium powder. The latter is mixed with a considerable excess of boric oxide and heated to bright redness. A vigorous reaction takes place and a mass is produced containing boric oxide, magnesium boride, magnesium borate and boron.

$$B_2O_3 + 3Mg = 3MgO + 2B$$
$$(3Mg + 2B = Mg_3B_2).$$

Long and repeated boiling with, first, dilute and then concentrated hydrochloric acid removes everything except the boron which, however, obstinately retains a little magnesium boride. On the commercial scale the product is heated in a vacuum in the electric furnace to 1,200°, which leaves fairly pure boron.

Crystalline boron of 99 per cent. purity has been made by passing condensed high-frequency sparks between electrodes of tungsten and molybdenum in an atmosphere of boron trichloride and hydrogen.

**462. Properties of Boron.**—The purest boron, made by the last method, has the appearance of a metalloid. It takes a good polish and then resembles a rather dark-tinted chromium. It is extremely hard. Its density is 2·3. It seems to be comparatively unreactive.

"*Amorphous boron*" forms a chestnut-coloured powder of density 2·45. Its melting point is high (*c.* 2,300° C.).

Though unaffected by air or oxygen at ordinary temperatures, it

burns brilliantly when heated in oxygen, forming boric oxide,

$$4B + 3O_2 = 2B_2O_3.$$

In air, boron nitride BN is also formed. Oxidising agents, such as nitric acid, concentrated sulphuric acid, potassium nitrate, etc., oxidise boron to boric acid.

With caustic alkalis hydrogen is evolved and a borate is produced.

The so-called *crystalline boron* is an aluminium boride. It forms intensely hard, very refractive crystals, or sometimes blackish or reddish foliate masses. It is much less reactive than amorphous boron, being hardly affected by oxygen even at high temperatures. It is oxidised by fused caustic potash and by fused lead chromate.

**463. Atomic Weight of Boron.**—The atomic weight of boron is evidently approximately 11 as shown by the vapour densities of its volatile hydrides, chlorides, organic compounds, etc. Dulong and Petit's law gives anomalous results. Since the equivalent is about 3·7 the element is tervalent. The exact determination has presented many difficulties. The change of weight when boron halides $BCl_3$, $BBr_3$ are converted into silver halides 3AgCl, 3AgBr, indicates a value close to 11·0 but probably a trifle less; the best value is probably 10·82.

There are two isotopes of atomic weight 10 and 11.

**464. Boron Compounds.**—Boron is always tervalent in its compounds; in its hydrides such as $B_2H_6$, it appears to be quadrivalent, but see § 472.

Its compounds are, in general, those of a non-metal. Thus its oxide is acidic in character; its chloride is a liquid hydrolysed by water. The only traces of metallic character are to be noticed in the formation of certain compounds with sulphur trioxide and phosphorus pentoxide (*e.g.*, boron phosphate $BO(H_2PO_4)$. These resemble salts in their formulæ, but do not appear to have their characteristic properties.

**465. Boric Oxide $B_2O_3$** is obtained by burning boron as described above (§ 462). It is much more easily prepared by heating boric acid to redness, when a colourless glass remains. When heated, it softens gradually and, like all glasses, has no definite melting point. Boric oxide is an acidic oxide, combining with water to form boric acids. Orthoboric acid is the chief product, but a little metaboric acid may also be present,

$$B_2O_3 + H_2O = 2HBO_2$$
$$HBO_2 + H_2O \rightleftharpoons H_3BO_3.$$

Boric oxide reacts with bases, forming borates, often brightly coloured (*v.* p. 388).

$$CuO + B_2O_3 = Cu(BO_2)_2.$$

Being non-volatile, boric oxide will displace such acids as sulphuric acid, nitric acid, etc., from their salts at temperatures above *c.* 500°C.

$$Fe_2(SO_4)_3 + 3B_2O_3 = 2Fe(BO_2)_3 + 3SO_3\uparrow$$

**466. Boric Acids.**—The following acids of boron are known, all derived from boron trioxide :—

Orthoboric acid, $H_3BO_3$, $B(OH)_3$ $(B_2O_3.3H_2O)$.

Metaboric acid $HBO_2$, $B(OH)O$, $(B_2O_3.H_2O)$.

Pyroboric acid $H_6B_4O_9$ $(2B_2O_3.3H_2O)$.

Tetraboric acid, $H_2B_4O_7$, $(2B_2O_3.H_2O)$.

Salts exist corresponding to all these and also to acids of formulæ $H_4B_6O_{11}$ and $H_2B_{10}O_{16}$.

Several *hypoboric acids, e.g.*, $H_4B_2O_4$, exist, derived directly or otherwise from the boron hydrides. They are reducing agents and rather unstable.

**467. Orthoboric Acid $H_3BO_3$.**—*Manufacture.*—Boric acid is found free in the *soffioni* or steam jets of volcanic origin which issue from the ground in certain districts of Tuscany. The steam, which contains only 0·05 per cent of boric acid, is taken from bore-holes, and is led through pipes which traverse boilers containing ordinary water. The natural steam is thus condensed and the steam raised in the boilers is used as a source of power. The condensed volcanic steam is evaporated, first in multiple evaporators, then in flat lead-lined cement pans, heated by the volcanic steam. The solution finally reaches a concentration of 10–12 per cent and is allowed to cool and crystallise. It is recrystallised from water once or twice and is then pure orthoboric acid.

Most of the world's boric acid is manufactured from native sodium or calcium borates found in California and Nevada.

The calcium borate is ground to powder and treated with boiling water. Sulphur dioxide is passed through the solution and boric acid and calcium sulphite are formed. The latter remains in solution,

$$Ca_2B_6O_{11} + 2SO_2 + 9H_2O = 2CaSO_3 + 6H_3BO_3.$$

The calcium sulphite dissolves in excess of sulphurous acid and the boric acid crystallises out.

Orthoboric acid forms white monoclinic crystals, greasy to the touch, and with a pearly lustre. It decomposes when heated (*v. infra*). Boric acid is appreciably volatile in steam. Boric acid

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is sparingly soluble in cold water but more freely in hot, 100 gms. of water dissolving 3·7 gms. of the acid at 12° C. and 28·1 gms. at 99·5° C.

Orthoboric acid is decomposed by heat, forming metaboric acid at 100° C. and tetraboric acid at 160° C.

$$H_3BO_3 = HBO_2 + H_2O$$
$$4HBO_2 = H_2B_4O_7 + H_2O.$$

Stronger heating causes the acid to swell to a frothy mass and then melt to a glassy mass of boron trioxide,

$$2H_3BO_3 = 3H_2O + B_2O_3.$$

Boric acid in solution is weakly acid to litmus, colouring it wine red. It colours yellow turmeric paper brown and alkalis blacken the brown stain. A brown coloration is also given to turmeric paper by alkalis, but the colour given by boric acid is not changed to yellow by dilute acids.

It finds a use in medicine as an antiseptic dusting powder (boracic powder) and mixed with soft paraffin wax as 'boracic ointment.' It has been greatly used as a food-preservative, being tasteless and probably harmless to adults. The Public Health Regulations of 1925 have forbidden the use of all food preservatives.

Boric acid is used in the making of certain glasses and glazes. Borate glazes are more fusible than silicate glazes, and have a higher co-efficient of expansion. This latter fact makes them useful for enamels which have to adhere to metals, the coefficients of expansion of which are, in general, greater than those of silicates.

**468. Other Boric Acids.**—*Metaboric acid* $HBO_2$.—Metaboric acid is prepared by heating orthoboric acid to about 100° C. for some time. It is a white solid, stable below 200° C., at which temperature it begins to give off water. Like orthoboric acid it is a very weak acid. When it dissolves in water orthoboric acid is formed.

$$HBO_2 + H_2O = H_3BO_3.$$

*Pyroboric Acid* $H_6B_4O_9$.—Pyroboric acid is also formed by heating orthoboric acid. Sodium pyroborate is made by melting borax with sodium carbonate,

$$Na_2B_4O_7 + 2Na_2CO_3 = Na_6B_4O_9 + 2CO_2.$$

Pyroboric acid forms orthoboric acid when it is dissolved in water,

$$H_6B_4O_9 + 3H_2O = 4H_3BO_3.$$

**469. Sodium Borates.**—*Sodium metaborate* $NaBO_2 . 4H_2O$ is known and may be prepared by the action of caustic soda on boric acid or borax,

$$NaOH + H_3BO_3 = NaBO_2 + 2H_2O$$
$$Na_2B_4O_7 + 2NaOH = 4NaBO_2 + H_2O.$$

It forms needle-shaped crystals.

The most important boron compound is another borate of sodium —borax.

**470. Sodium Tetraborate[1], Borax $Na_2B_4O_7$.**—*Preparation.*—Borax is extracted commercially from the salt deposits at Searles Lake, California, and to some extent by recrystallising the native mineral *kernite*, $Na_2B_4O_7 . 4H_2O$, which is found in the same region.

Borax is also prepared to a diminishing extent from Italian boric acid. The acid, after preliminary purification, is boiled with crude soda-ash,

$$Na_2CO_3 + 4H_3BO_3 = Na_2B_4O_7 + 6H_2O + CO_2,$$

and the product crystallised and recrystallised.

*Properties.*—Borax exists in three forms :—

(1) *Borax glass*, the anhydrous product produced by heating ordinary borax above its melting point until no more steam is evolved. It forms a colourless glass which absorbs moisture from the air and forms the decahydrate.

(2) *Ordinary or Prismatic Borax.*—This is the decahydrate, $Na_2B_4O_7.10H_2O$. It forms large and colourless monoclinic crystals, which have a 'cooling' taste. Borax is sparingly soluble in cold water but quite soluble in hot. At 21·5° C. 100 gms. of water dissolve 2·8 gms. of anhydrous borax, and at 100° 52·3 gms.

When heated, borax loses water, first melting in its water of crystallisation, then swelling into a white voluminous spongy mass of anhydrous borax, which then fuses to the colourless glass described above. If traces of metallic oxides or salts be mixed with the borax, the borates of these metals are formed and dissolve in the fused borax, forming beads of 'borax glass' of characteristic colours. This serves as a test for certain metals.

The test is best performed by moistening a platinum wire and taking up a little borax upon it. This is heated in the Bunsen flame, keeping the bead of melted borax on the *far* side of the flame. It is better not to make a loop, as bending and unbending soon breaks the wire. When the bead is formed it will be colourless. It is moistened with a little of a solution of the substance to be examined or a few grains of the powdered substance may be attached to the moistened bead. On re-heating, the bead shows the characteristic colours given in the table below. The 'oxidising flame' is the exterior of the Bunsen flame, the reducing flame is the interior. Beads heated in the reducing flame should be cooled in the cold reducing

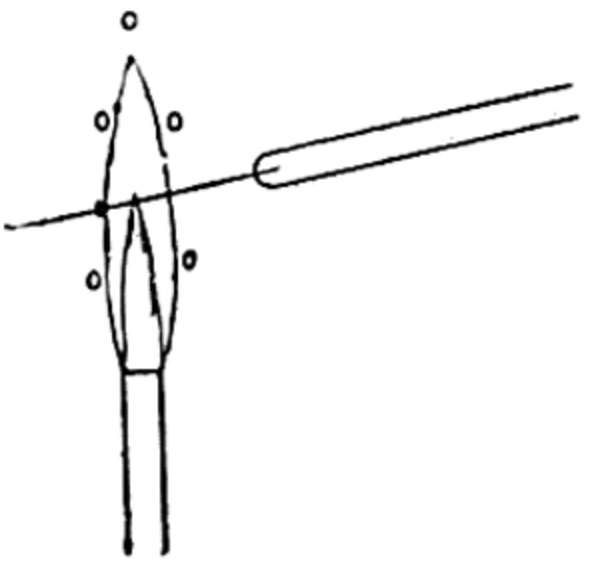


Fig. 95.—The borax bead.

[1] Also called 'diborate' and 'pyroborate.' The nomenclature of these acids is still unsystematic.

| Metal in compound added | Colour of Bead in | | | |
|---|---|---|---|---|
| | Reducing Flame. | | Oxidising Flame. | |
| | Hot. | Cold. | Hot. | Cold. |
| Copper . . . | Colourless. | Opaque. brown-red. | Blue. | Blue-green. |
| Iron . . . | Bottle-green. | Bottle-green. | Brown-yellow. | Yellow. |
| Chromium . . | Green. | Green. | Yellow. | Yellowish-green. |
| Manganese . . | Amethyst. | Violet. | Colourless. | Colourless. |
| Cobalt . . . | Blue. | Blue. | Blue. | Blue. |
| Nickel . . . | Grey. | Grey. | Violet. | Brownish. |
| Lead, silver, and some easily reducible metals . . | Greyish or blackish. | | Colourless. | |

atmosphere of coal gas in the centre of the flame.

If a platinum wire is not available a glass rod is a very fair substitute.

(3) *Octahedral borax* $Na_2B_4O_7.5H_2O$ is made by crystallising borax at about 60° C. It forms regular octahedra.

Solutions of borax are weakly alkaline and can be titrated like sodium carbonate, using methyl orange as an indicator.

Borax is decomposed by acids, boric acid being precipitated,

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3.$$

Borax is used in a large number of trades. It is employed for making glazes containing borates for tiles and pottery (p. 471). It is also used for making enamels; as a flux for soldering and welding; as a cleaning agent in laundry and soap-making; for curing hams; for glazing paper, playing cards, linen, etc. This type of glaze, of course, has nothing to do with the glazes obtained by fusion on pottery, etc.

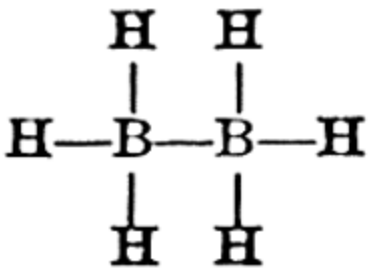
**471. Sodium Perborate** is the salt of an acid, $HBO_3$, which is not known in the free state. The salt is prepared by the action of sodium peroxide on boric acid, suspended in cold water. A salt, 'perborax,' crystallises out on standing, and this, when treated with a dilute acid, gives a precipitate of sodium perborate, $NaBO_3.4H_2O$.

$$Na_2O_2 + 4H_3BO_3 = Na_2B_4O_8 + 6H_2O$$
$$Na_2B_4O_8 + HCl + 4H_2O = NaBO_3 + NaCl + 3H_3BO_3.$$

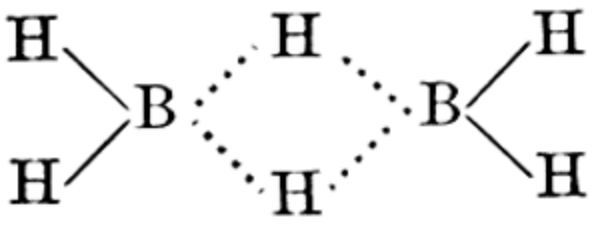
Sodium perborate is a strong oxidising agent, behaving in solution like a mixture of borate and hydrogen peroxide. It is used as a cleanser, especially for dentures, having the alkaline properties of borax and the bleaching power of hydrogen peroxide.

**472. Boron Hydrides.**—Numerous hydrides of boron exist and may be obtained by the action of acids upon magnesium boride. These include

$B_2H_6$, $B_4H_{10}$, $B_6H_{10}$, $B_{10}H_{14}$, $B_5H_9$, $B_6H_{12}$. The chief product of the reaction is $B_4H_{10}$, which soon breaks up into $B_2H_6$, and hydrogen. The constitution of the hydride $B_2H_6$ is peculiar. The formula could be written as I.



I.



II.

if boron were quadrivalent, but its place in the Periodic table and the formulæ of its other compounds make us think it tervalent. Its structure has been formulated as II., and in favour of this formula is the great instability of these compounds, in which two of the hydrogen atoms are linked, we suppose, by a single electron only.

The hydrides of boron are for the most part very unstable gases, losing hydrogen even at a low temperature and having strong reducing powers.

**473. Other Boron Compounds.**—*Boron carbide* $B_4C$, is made from boric oxide and coke in the electric furnace at 2600° C. It is the hardest abrasive ever made artificially, and therefore finds special uses in such articles as nozzles for sand blasting.

$$2B_2O_3 + 7C \rightarrow B_4C + 6CO$$

*Boron nitride* BN is a white amorphous and inert powder, made by heating boron in an atmosphere of nitrogen.

*Boron sulphide* $B_2S_3$ forms white needles, melting at 310° C. It may be made by the action of sulphur on amorphous boron.

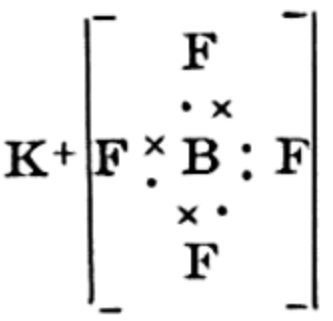
*Boron trifluoride* $BF_3$ is a gas formed by the action of sulphuric acid and a fluoride on boron trioxide,

$$CaF_2 + H_2SO_4 = CaSO_4 + H_2F_2$$
$$B_2O_3 + 3H_2F_2 = 2BF_3 + 3H_2O.$$

It is a colourless fuming gas, which reacts with water with great vigour, forming metaboric and *hydrofluoboric acids*,

$$8BF_3 + 4H_2O = H_2B_2O_4 + 6HBF_4..$$

The latter acid forms stable borofluorides, such as $KBF_4$. In these boron is not pentavalent, the formula being



*Boron trichloride* $BCl_3$ is made by the action of chlorine on heated amorphous boron. The vapours are condensed in a well-cooled U-tube.

It is a volatile, colourless, mobile, fuming liquid, boiling at 18·2° C.

It is decomposed by water, forming boric and hydrochloric acids,

$$BCl_3 + 3H_2O = H_3BO_3 + 3HCl.$$

**474. Detection of Boron.**—Boron is nearly always found as boric

acid or borate. If in any other state the action of hot concentrated nitric acid will convert it into the former compounds.

Boric acid and borates are recognised by their formation of a glass when heated, though they are not the only substances to do this. They are detected by heating the suspected substance with a little sulphuric acid, adding alcohol and setting fire to it. A green-edged flame, due to ethyl borate, indicates boron, which gives three conspicuous lines in the green of the spectrum and one in the blue.

*Estimation.*—Boric acid may be titrated with caustic soda, with phenol-phthalein as indicator if glycerol be present. Borax may be titrated with a mineral acid (p. 388).

## ALUMINIUM Al, 26·97

**475. History.**—Certain compounds of the element, aluminium, have been known from the earliest times. Alum, potassium aluminium sulphate, was known to the Greeks and Romans, while the crystallised oxide, ruby and sapphire, have been used from a remote period as gem stones. The existence of an 'earth,' alumina, as distinct from lime, etc., was recognised in the eighteenth century, and the metal was prepared by Oersted and Wöhler in 1824 and 1827, probably in an impure state. Bunsen and Deville both obtained the metal by electrolysis of the fused chloride in 1854. The modern electrolytic process came into use in 1886 and developed very rapidly after the establishment of the automobile industry.

**476. Occurrence.**—Aluminium is found in very great quantities in the earth's crust, being only less common than oxygen and silicon. Its commonest form is as silicate, associated with silicates of potassium, calcium, etc., in *felspar*, which is a constituent of most igneous rocks.

Aluminium silicate gives the 'sticky' quality to clays. Other aluminium minerals include the oxide as *bauxite*, *diaspore*, *corundum*, *ruby*, *sapphire*, the sulphate associated with potassium sulphate in *alumstone*, the fluoride in *cryolite*, the double fluoride of sodium and aluminium. Numerous aluminates also occur, the most important of which are the *spinels*. Ordinary spinel is magnesium aluminate; iron and manganese spinels also occur.

The chief sources of the metal are bauxite and cryolite.

### 477. Manufacture of Aluminium.

*Deville's Process.*—Up to 1886, aluminium was made by the action of sodium on the double chloride of aluminium and sodium,

$$AlCl_3 + 3Na = Al + 3NaCl.$$

This process produced aluminium at about £1 a pound, and was rendered obsolete by the electrolytic process.

*Electrolytic Process.*—This process can only be carried on where water power is available and electricity is cheap. The source of aluminium is the oxide which is found as bauxite $Al_2O_3.2H_2O$. This mineral contains some considerable quantity of iron and silica, which must be removed before the aluminium is extracted. The usual process is to dissolve it in caustic soda solution under pressure. The iron oxide does not go into solution, but the alumina forms soluble sodium aluminate and the silica, sodium silicate. The

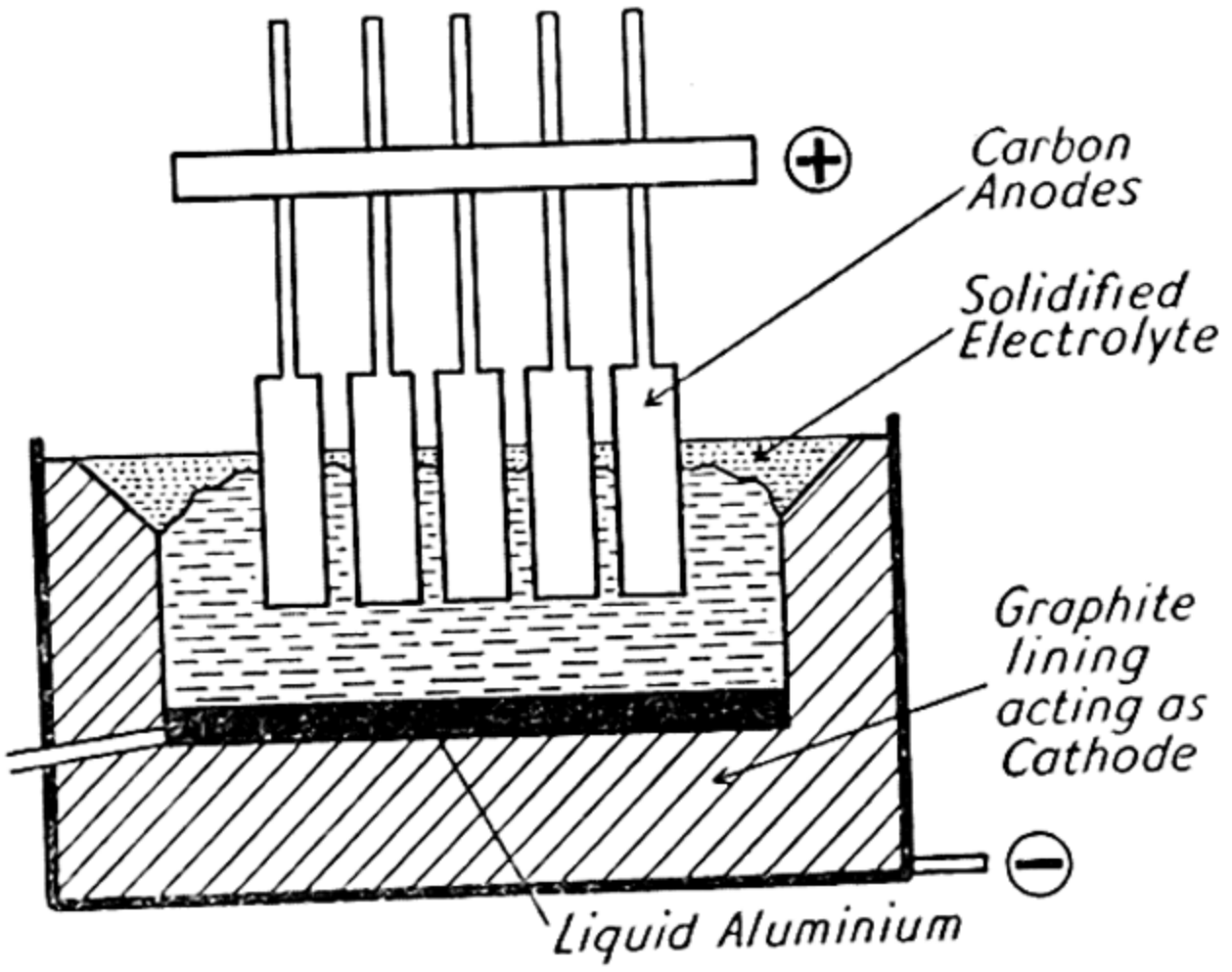



Fig. 96.—Manufacture of aluminium by electrolysis.

sodium aluminate dissolves a considerable further quantity of alumina probably as a colloidal solution,

$$(2+n)\underset{\text{Solid}}{Al_2O_3} + 2NaOH + (n-1)H_2O = 2NaAlO_2 + \underset{\text{Colloidal.}}{2nAl(OH)_3}$$

This liquid is filtered through presses and the aluminium hydroxide present as colloidal solution is precipitated by addition of some of the previous batch of purified aluminium hydroxide. It is then filtered off, pressed, and heated to convert it into oxide. The liquid containing sodium aluminate is used to dissolve more bauxite.

The aluminium oxide, prepared as above, is then added to a bath consisting of melted cryolite, *i.e.*, sodium aluminium fluoride (p. 401), contained in a large electrolytic cell (Fig. 96), of which the anodes are carbon blocks and the cathode the graphite lining of the cells. The cryolite is electrolysed,

$$AlF_3 = Al + 3F,$$

the fluorine combining at once with the alumina present,

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$$2Al_2O_3 + 12F = 4AlF_3 + 3O_2,$$

and thus restoring the aluminium fluoride decomposed. The aluminium collects at the bottom of the cell and is tapped off from time to time.

**478. Physical Properties.**—Aluminium is a white metal. It has, when scraped, a brilliant lustre, which is soon dulled by formation of a thin layer of oxide.

Aluminium melts at 660° C. Its density is 2·70 and it is the lightest metal which can be employed for machine parts, etc. It finds numerous uses, particularly in automobile and aeroplane engineering, where it is used for crank cases and other machine parts which are required to be light and strong without being particularly hard or heat-resistant.

The specific heat of aluminium is 0·21, and its atomic heat is thus a little lower than would be predicted by Dulong and Petit's law ($0·21 \times 27 = 5·67$, *v.* § 63).

Aluminium is a very good conductor of heat and electricity and *weight for weight* is a much better conductor than copper.

The film of oxide which forms on the surface of the metal makes it very difficult to solder, and it is nearly always welded by means of the oxygen blowpipe or the electric arc.

**479. Chemical Properties.**—Bright aluminium is at first oxidised rapidly, but the thin film of oxide produced has a very strong protective action. Aluminium is therefore very little affected by oxygen. The metal, if heated sufficiently in a finely-divided condition, will burn with the production of much heat and brilliant light,

$$4Al + 3O_2 = 2Al_2O_3.$$

Aluminium is attacked by chlorine, giving the chloride (*q.v.*), and bromine acts similarly,

$$2Al + 3Cl_2 = 2AlCl_3.$$

Aluminium is not attacked by water unless the coating of oxide is prevented from forming. If aluminium is amalgamated by scraping it and rubbing it with mercury or mercurous nitrate it reacts easily and rapidly with water, decomposing it even in the cold.

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2.$$

The purest metal available is very slowly attacked by the halogen acids, which however attack commercial aluminium readily, forming hydrogen,

$$2Al + 6HCl = 2AlCl_3 + 3H_2.$$

Nitric acid and sulphuric acid hardly affect it. Strong hot sulphuric

acid reacts to some extent, giving sulphur dioxide and aluminium sulphate.

Aluminium is readily attacked by alkalis, which form aluminates and hydrogen,

$$2KOH + 2Al + 2H_2O = 2KAlO_2 + 3H_2.$$

Aluminium vessels are therefore damaged by hot soda solution.

Aluminium displaces many metals from their salts, more especially the chlorides.

**480. Aluminothermic Processes.**—Aluminium reacts very vigorously with oxygen compounds at high temperatures. On this fact is based the aluminothermic method of preparing metals. If a mixture of the oxide of a metal (*e.g.*, ferric or chromic oxide) and coarse aluminium powder is placed in a resistant crucible and ignited

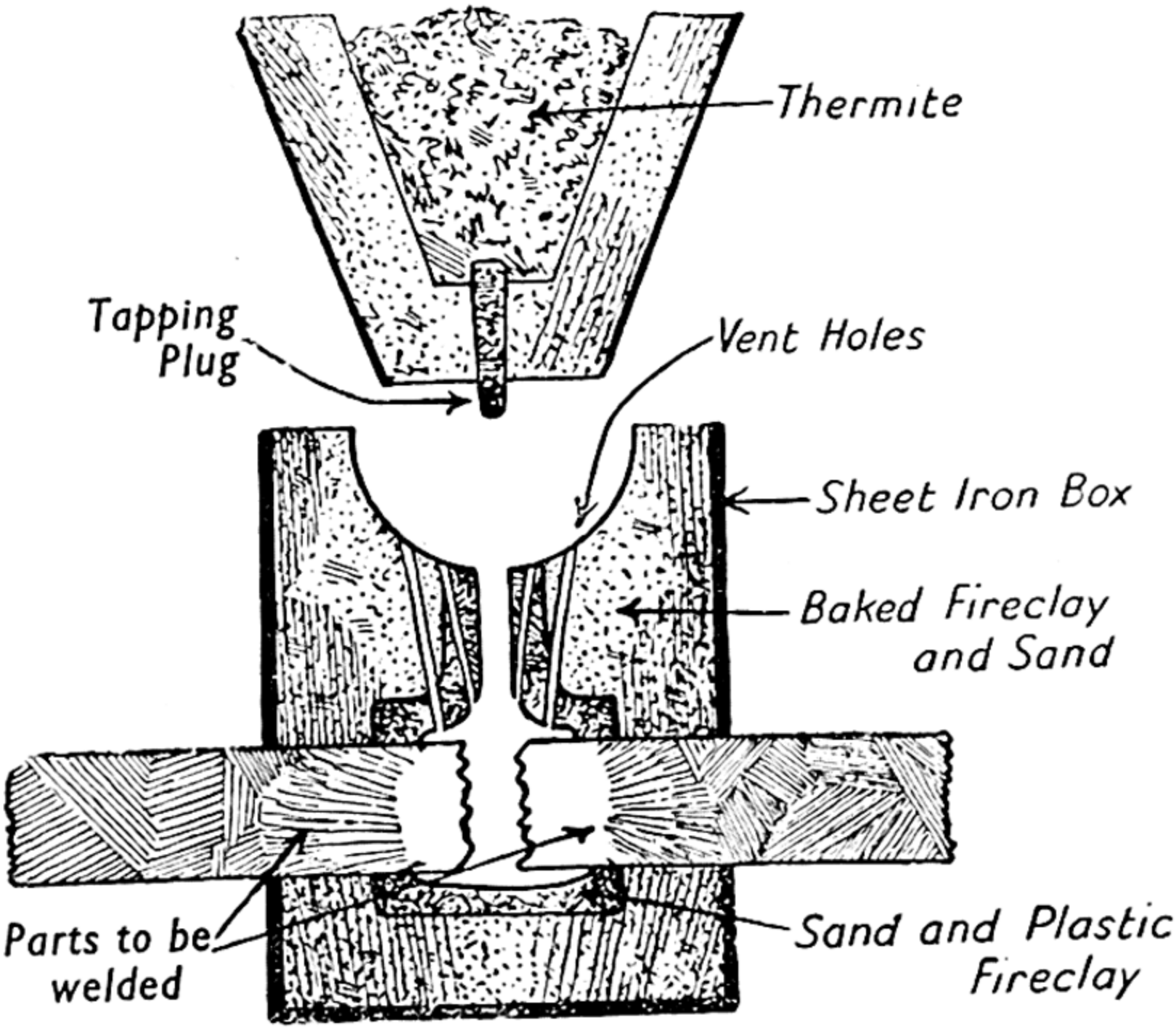


FIG. 97.—Welding by thermite.

by means of a piece of magnesium ribbon stuck into the mass, a violent reaction occurs, the temperature rising to a white heat. The metal is liberated and sinks to the bottom of the crucible, and the aluminium oxide simultaneously produced fuses and then solidifies to an upper layer of hard slag.

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe.$$

The method is applied to the manufacture of chromium, manganese, tungsten, etc. (*q.v.*, §§ 978, 1107).

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A mixture of aluminium powder and iron oxide, together with some steel as turnings or punchings, is known as thermite, and when fired as above produces liquid steel at a temperature of about 2,500° C. It is used for welding machine parts, etc., *in situ*. A mould is built up round the parts (Fig. 97) and the thermite is placed in a crucible lined with magnesia and provided with a tapping plug. The thermite is fired, and by knocking out the plug the steel is allowed to run into the mould, where it melts the broken parts into a homogeneous mass of iron or steel.

Thermite is also employed in incendiary bombs.

**481. Uses and Alloys.**—Because of its lightness and its great strength when alloyed, aluminium is widely used in the making of machine parts, particularly in connection with transport. It is second only to copper amongst the common metals for its electrical conductivity, and is therefore widely used in the electrical industry, particularly in the construction of high-tension cables. The most important alloys of aluminium are *Dural*, containing Al, 94 per cent.; Mn, 1 per cent.; Mg, 1 per cent.; Cu, 4 per cent.; *Magnal*, containing about 8 per cent Al, and 92 per cent. Mg, together with traces of manganese and zinc, and *aluminium bronze*, containing 3–10 per cent. of aluminium and 90–97 per cent. of copper. All of these alloys are superior to the pure metals in strength, hardness, and resistance to corrosion. The technique of *anodising* considerably enhances the resistance of aluminium and its alloys to corrosive agents. The object to be treated is made the anode of an aqueous electrolytic cell. Oxygen is discharged by the electric current and attacks the aluminium, forming a transparent but impervious coating of the oxide, which affords an excellent protection against further chemical attack.

**482. Atomic Weight of Aluminium.**—Dulong and Petit's law and the vapour density of the chloride above 1,000° C. and of certain organic compounds indicate an atomic weight of approximately 27. The equivalent is 9 and the valency therefore is 3. The exact atomic weight has been computed from the volume of hydrogen evolved when the metal is treated with acids or alkalis, and also from the weight of silver chloride or bromide formed from a given weight of aluminium chloride or bromide. The latter method is the most accurate. The best value is probably 26·97.

**482a. Aluminium Hydride.** $(AlH_3)n$ is white and non-volatile.

**483. Aluminium Oxide.**—There is only one oxide of aluminium—alumina $Al_2O_3$. It occurs native as crystals, pure and colourless in *corundum* or white sapphire, coloured in *sapphire*, *ruby* and *oriental topaz*, which are valued as gems on account of their beauty of colour and hardness. An impure form of the oxide is known as *emery*. Alumina also occurs native in the hydrated state as the important

mineral, bauxite. Aluminium oxide is prepared by heating aluminium hydroxide or, better, ammonium alum (§ 496). The commercial process of preparation from bauxite is described in § 477. As obtained by carefully heating the hydroxide, it is a soft white amorphous powder, easily soluble in acids, but after heating to redness it becomes very hard and practically insoluble in all acids.

Alumina may be melted in the oxyhydrogen flame and it may be crystallised, forming crystals which, if pure, are identical with corundum, and if coloured with traces of chromium or cobalt are identical with rubies and sapphires.

Verneuil has devised an ingenious piece of apparatus, which is used for making these artificial gems. An inverted oxyhydrogen blow-pipe plays on a small rod of alumina, which serves as a support for the gem which is to be produced. Into the flame is caused to fall finely-powdered alumina with a little chromium oxide. The particles melt at the very high temperature of the flame and, sticking to the alumina rod, build up a pear-shaped ruby, consisting of a single crystal. The ruby is indistinguishable from the natural gem except in that its flaws, if any, are curved rather than straight.

Aluminium oxide, fused in the electric furnace, is known as *alundum*. It is used as an abrasive and also for making refractory crucibles, muffles, firebricks, etc.

Aluminium oxide is a very stable and unreactive substance. The oxide, after ignition, is dissolved only after prolonged boiling with hydrochloric acid. It is, however, dissolved by caustic alkalis, forming aluminates,

$$Al_2O_3 + 2KOH = 2KAlO_2 + H_2O.$$

Aluminium oxide is not reduced to the metal by either hydrogen or carbon. The heat of combustion of aluminium is so high that its compound with oxygen—alumina—is only reduced with great difficulty.

**484. Aluminium hydroxide** probably exists as $Al(OH)_3$, and also as $AlO(OH)$. It is readily obtained as a gelatinous precipitate by the action of ammonia or other alkali on an aluminium salt,

$$Al_2(SO_4)_3 + 6NH_4OH = 2Al(OH)_3 + 3(NH_4)_2SO_4.$$

When freshly precipitated it readily dissolves in acids, forming aluminium salts, but after standing dissolves with difficulty.

It dissolves in caustic soda (but not in ammonia), forming the aluminate,

$$AlO(OH) + NaOH = NaAlO_2 + H_2O.$$

Aluminium hydroxide has a remarkable power of combining with organic colouring matters, forming coloured substances called 'lakes.' Thus, if a solution of cochineal in weak alkali is mixed with a solution of alum the precipitated aluminium hydroxide

combines with the cochineal, forming the beautiful red 'lake' known as carmine and much used as a pigment. The property is also used in dyeing. Thus cotton may be soaked in a solution of aluminium acetate (or sodium aluminate) and, when impregnated with the salt, may be exposed to warmth and moisture, when aluminium hydroxide is formed by hydrolysis (§ 121). The cotton may then be dyed in such a dye as alizarin (madder), and a fine bright permanent red is obtained. If the cotton is not treated with an aluminium compound the dye does not adhere and may be wholly washed out again. Ferric salts and chromium salts may also be used in place of those of aluminium and produce different shades.

**485. Aluminates.**—Sodium and potassium aluminates are prepared by the action of caustic alkalis on alumina as above. They are made on the large scale by heating bauxite with caustic alkali solution under pressure. They are probably to be regarded as salts of the acid, $Al(OH)_3 . H_2O$ or $HAl(OH)_4$. Their formulæ are commonly written $NaAlO_2$ and $KAlO_2$.

The aluminates of the alkalis are soluble in water. Their solutions are easily hydrolysed and on dilution precipitate aluminium hydroxide,

$$NaAlO_2 + 2H_2O = Al(OH)_3 + NaOH.$$

Solutions of these salts are therefore strongly alkaline. Acids also precipitate the hydroxide,

$$KAlO_2 + HCl + H_2O = KCl + Al(OH)_3.$$

The aluminates are decomposed when boiled with ammonium chloride, aluminium hydroxide being precipitated.

$$NaAlO_2 + NH_4Cl + H_2O = NaCl + NH_3 + Al(OH)_3.$$

This fact is utilised to distinguish aluminium from zinc in some systems of qualitative analysis, for zincates are not so decomposed.

**486. Salts of Aluminium.**—Aluminium salts, in general, are colourless and non-poisonous. They are distinguished by their ready hydrolysis by water, aluminium in this respect showing a decided non-metallic character. Thus the chloride and sulphide behave in this respect like the compounds of a non-metal or metalloid.

Aluminium salts, in virtue of the trivalent ion, $Al^{+++}$ which they produce, have a remarkable power of precipitating colloids.

Aluminium hydroxide, being a very weak base, does not form stable salts with very weak acids. Thus aluminium carbonate does not exist. The chemistry of aluminium in general may be instructively compared with that of arsenic or quadrivalent tin, each the first metal or metalloid of a group.

Solutions containing the aluminium ion display but few precipitation reactions. With alkalis and with salts which hydrolyse, forming some alkali (*e.g.*, sodium carbonate or sulphide), a precipitate of gelatinous aluminium hydroxide is produced,

$$Al^{+++} + 3OH^- = Al(OH)_3 \downarrow .$$

This precipitate is soluble in excess of caustic soda (§ 484) forming sodium aluminate.

**487. Aluminium Carbide $Al_4C_3$** is made by heating a mixture of alumina and carbon to a very high temperature,

$$2Al_2O_3 + 9C \rightleftharpoons Al_4C_3 + 6CO.$$

It forms a yellowish powder, which is decomposed by water or dilute acids, forming methane,

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4.$$

*Aluminium carbonate* does not exist.

**488. Aluminium Silicates.**—Aluminium silicate enters into the composition of numerous minerals. Among these may be mentioned the felspars, which are minerals of great importance and form a part of most igneous rocks.

*Orthoclase*, potash felspar, is $KAlSi_3O_8$ ($K_2O.Al_2O_3.6SiO_2$). *Albite* is the corresponding sodium compound.

The *micas* are double silicates of aluminium and another metal, usually magnesium or iron.

*Garnets* are double silicates of a trivalent metal, often aluminium, and a divalent metal, such as calcium, magnesium or ferrous iron.

The *zeolites* are hydrated double silicates of a metal and aluminium. The zeolite, *sodium permutit*, $Na_2O.Al_2O_3.2SiO_2.6H_2O$, is used in softening water. The native material is used by some manufacturers of water softeners, whilst others use an artificial product made by heating china clay, sodium carbonate and silica.

**489. Clays.**—The term clay denotes certain earths which are highly plastic when wet and which, when heated to redness, lose their plasticity and are converted into a hard mass unaffected by water.

Clay is not a single substance but consists of very fine particles of quartz, silica, felspar, mica, etc., resulting from the decomposition of certain igneous rocks such as granite, bound together by a sticky substance which appears to be a hydrated aluminium silicate, $Al_2O_3.2SiO_2.2H_2O$. Clays originally formed by the decomposition of these rocks may either be found in their original position, as is china clay, or may be carried by water and deposited at a distance, as are brick-earth, etc.

The value of clays in industry depends on their plasticity while moist, which enables them to be formed into complex shapes, and their subsequent hardening under the action of heat to a stony or glassy mass which is proof against the action of water.

When moist clay is dried at 100° C. it loses most of its water and becomes hard and brittle. If this product is soaked in water it once more becomes soft and plastic. At about 500°–600° C. a

further change takes place, *combined* water is driven off and a hard porous mass, which does not soften in water, is left. At temperatures above a red heat, 900°–1,000° C., most clays becomes less porous and more stony in consistence, and at temperatures between *c.* 1,400°–1,850° C. they melt to a glassy mass.

*Kaolin* or *china clay* is a white earthy substance, less plastic and sticky than most clays. It consists of aluminium silicate ($Al_2O_3.2SiO_2.2H_2O$) with some quartz, sand and mica. These latter are commonly removed from it by washing. China clay is used for the finer porcelains and earthenwares and also for 'filling' white papers, etc.

*Ball clay* is a less pure material used for the manufacture of earthenware.

*Common clay* contains more impurities, among which is usually iron oxide, which gives a red colour to the burnt material. It is used for the cheaper pottery, bricks, tiles, etc.

*Fireclay* contains a good deal of silica, and very little iron. When fired it forms a material of high fusing point—1,500° C. and upwards.

**490. Aluminium Nitrate $Al(NO_3)_3.9H_2O$,** is a colourless crystalline salt extremely soluble in water. When heated it decomposes in the same way as other nitrates (§ 750).

**491. Aluminium Sulphide $Al_2S_3$.**—Aluminium sulphide is made by the reaction of aluminium and sulphur. It is at once decomposed by water,

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S,$$

hydrogen sulphide being evolved. It is therefore not precipitated from solutions of aluminium salts when these are treated with hydrogen sulphide—a fact of importance in qualitative analysis. When alkaline sulphides are added to aluminium salts the hydroxide is precipitated in place of the sulphide.

**492. Aluminium Sulphate $Al_2(SO_4)_3 . 18H_2O$.**—This salt is found native in the form of an efflorescence and is called *hair-salt* or *feather alum*.

It is made by the action of sulphuric acid on bauxite or on china clay, aluminium silicate,

$$Al_2Si_2O_7 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O + 2SiO_2$$

The clay is heated and then treated with the acid.

The solid product is extracted with water in order to separate the aluminium sulphate from silica, unchanged clay, etc., and the solution so obtained is crystallised.

Aluminium sulphate forms ill-defined crystals, containing no less than eighteen molecules of water of crystallisation. The commercial salt is not, however, fully hydrated.

The salt is very soluble in water.

When it is heated, water is at first lost and then at a red heat alumina and sulphur trioxide are produced,

$$Al_2(SO_4)_3 = Al_2O_3 + 3SO_3.$$

Aluminium sulphate forms an important series of double salts known as the alums (§ 493).

Aluminium sulphate has a remarkable power of precipitating colloids (§ 95), and is used in purifying sewage. It finds a use also in 'foam' fire extinguishers. These contain aluminium sulphate and a bicarbonate in separate receptacles. When they mix, a stable foam of bubbles of carbon dioxide is produced.

$$Al_2(SO_4)_3 + 6NaHCO_3 = 2Al(OH)_3 + 3Na_2SO_4 + 6CO_2,$$

the aluminium hydroxide formed causing the bubble walls to be stable. These extinguishers are effective for burning oils. Oils float on water but the light foam floats on burning oil and excludes the air.

**493. The Alums.**—The name 'alums' is given to the members of a group of double salts which have the general formula,

$M'_2SO_4.M'''_2(SO_4)_3.24H_2O$, or better $M'[M'''(SO_4)_2].12H_2O$, where M′ is a monovalent metal or group of atoms (Li, K, Na, Rb, Cs, $NH_4$, — $N_2H_5$, — $NH_3OH$, Tl′, but not Ag, Hg′, or Cu′) and M‴ a tervalent metal (Al, Cr, Fe‴, Mn‴, Co‴, V‴, Ti‴, Ga, In, but not Bi, Tl‴ or the rare earths); $SeO_4''$ may replace $SO_4''$.

Examples of alums are :—

| | |
|---|---|
| $KAl(SO_4)_2.12H_2O$ . . | Potash or common alum. |
| $NH_4Fe(SO_4)_2.12H_2O$ . . | Iron ammonium alum. |
| $RbCr(SO_4)_2.12H_2O$ . . | Rubidium chrome alum. |

The alums all crystallise in the cubic system with twelve molecules of water and form well-marked octahedra or cubes. The alums which do not contain aluminium are considered under the heading of the sulphate of the tervalent metal contained in them (*v.* §§1000, 1169).

**494. Potassium Aluminium Sulphate, Potash Alum, $KAl(SO_4)_2 \cdot 12H_2O$.**—This salt is occasionally found as an efflorescence. The *alun de plume*, found in the island of Melos, was known to the Romans and Greeks, who also prepared the salt from alumstone.

Alum is made from *alunite* or *alumstone*, a mineral of the composition $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$, which occurs in Italy, Hungary, the Greek Archipelago, and other places. It is probably derived from felspars which have been subjected to the action of sulphurous volcanic gases.

The alunite is calcined and then treated with sulphuric acid. Some potassium sulphate is added and the alum is allowed to crystallise,

$$K_2SO_4.Al_2(SO_4)_3 + 4Al(OH)_3 + 6H_2SO_4 = K_2SO_4 + 3Al_2(SO_4)_3 + 12H_2O$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O = 2KAl(SO_4)_2.12H_2O.$$

Alum is also made from pyritic shale, which is a hardened clay, containing pyrites ($FeS_2$). The oxidation of the latter yields ferrous sulphate and sulphuric acid, which converts the aluminium silicate of the clay into aluminium sulphate. The shale is roasted and extracted with water. Potassium chloride is then added to the solution containing ferrous, ferric and aluminium sulphates. The reactions,

$$FeSO_4 + 2KCl \rightleftharpoons FeCl_2 + K_2SO_4,$$

and $$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O = 2KAl(SO_4)_2 . 12H_2O$$

result in the crystallisation of alum, which is then recrystallised.

Alum is also made commercially from aluminium sulphate prepared from bauxite.

In the laboratory any of the alums may be made by mixing the requisite quantities of concentrated solutions of the two sulphates in question and, if need be, evaporating. The alum crystallises out.

Alum forms colourless octahedra, which may be grown to great sizes. The crystals are neither efflorescent nor deliquescent. It has a peculiar and sweetish astringent taste. Alum is moderately soluble in cold water but very soluble in hot.

| *Temperature °C.* | *Gms. of potassium alum dissolved by 100 gms. water.* |
|---|---|
| 0 | 3·9 |
| 20 | 15·1 |
| 40 | 30·9 |
| 60 | 66·6 |
| 80 | 134·5 |
| 100 | 357·5 |

When heated to 92·5° C. alum melts in its water of crystallisation. Further heating results in the loss of water, the anhydrous salt, known as *burnt alum*, remaining. Above a red heat the aluminium sulphate itself decomposes, leaving behind aluminium oxide (§§ 492, 938).

When treated with caustic soda or potash, aluminium hydroxide is precipitated and, on further addition of alkali, redissolves (§ 484). Ammonia precipitates alumina but does not redissolve the precipitate.

*Uses.*—Alum is used as a mordant in dyeing (§ 484), in leather manufacture and for fireproofing inflammable fabrics. Its power of precipitating colloidal substances gives it a minor use as a 'styptic' for stopping bleeding from small cuts, the blood from which it

coagulates. This property is shared by the salts of all tervalent metals, notably ferric salts.

**495. Soda Alum $Na_2SO_4 . Al_2(SO_4)_3 . 24H_2O$** much resembles potash alum and can be made by mixing sodium sulphate solution saturated at 45° C., with the requisite weight of aluminium sulphate contained in insufficient water to dissolve it. It is very soluble in water, which dissolves its own weight of the salt. In other respects it resembles potash alum.

**496. Ammonium Alum $(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24H_2O$** is prepared by mixing solutions of the sulphates of aluminium and ammonium. It resembles potash alum in most particulars. When strongly heated it leaves a residue of pure alumina,

$$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O = (NH_4)_2SO_4\uparrow + 24H_2O\uparrow + 3SO_3\uparrow + Al_2O_3.$$

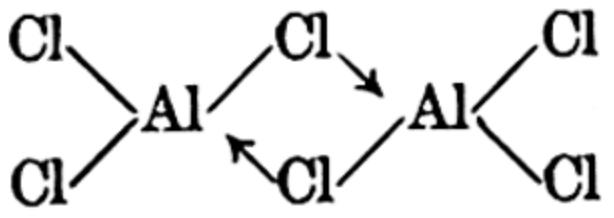
*Rubidium and cæsium alums* are very sparingly soluble in water (1·81 and 0·49 gm./100 gms. aq.). They are therefore useful in purifying these elements.

**497. Aluminium Fluoride $AlF_3$,** in the form of sodium alumini-fluoride $Na_3AlF_6$ (or $AlF_3.3NaF$), occurs as the mineral *cryolite*, which is found in quantity only in one locality in Greenland. It finds a considerable use in the manufacture of aluminium (§ 477).

**498. Aluminium Chloride $Al_2Cl_6$.**—Aluminium chloride is prepared in the anhydrous condition by passing a stream of chlorine or hydrogen chloride over heated aluminium contained in a wide tube. The volatile aluminium chloride may be condensed in a wide-mouthed bottle and stoppered as soon as the reaction is complete,

$$2Al + 3Cl_2 = 2AlCl_3.$$

On the commercial scale chlorine is passed over a mixture of alumina and carbon. A solution of the salt is made by the action of hydrochloric acid on aluminium. When the solution is concentrated, crystals of the dodecahydrate, $Al_2Cl_6.12H_2O$, are formed. The anhydrous salt is a white solid which sublimes below 200° C. Its vapour density at low temperatures indicates the formula, $Al_2Cl_6$, the structure of which is :—




Both the anhydrous salt and the hydrate are very hygroscopic. The anhydrous salt fumes in air, owing to the formation of hydrogen chloride by its reaction with the moisture of the air. The salt when treated with water forms aluminium hydroxide and hydrogen chloride. A solution of the salt can only exist in presence of much free hydrochloric acid,

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl.$$

Anhydrous aluminium chloride finds great use in the Friedel-

Crafts condensation reactions which are much used in organic chemistry.

**499. Aluminium Bromide $AlBr_3$** is made by the direct action of bromine on aluminium. It resembles the chloride in most respects.

**500. Detection and Estimation of Aluminium.**—Aluminium salts are distinguished by giving no precipitate with hydrogen sulphide in acid solution, while giving a white gelatinous precipitate of aluminium hydroxide with ammonia in presence of ammonium chloride. This precipitate is soluble in caustic soda (§ 484).

Aluminium is estimated by precipitating the hydroxide as above, filtering this off, igniting it and weighing it as the oxide.

Zinc salts give somewhat similar reactions to the above, but zinc hydroxide is not precipitated in presence of ammonium chloride. Moreover, the solution of sodium aluminate gives a white precipitate of the hydroxide when boiled with ammonium chloride, which sodium zincate does not; and sodium zincate gives a white precipitate of the sulphide with hydrogen sulphide, which the aluminate does not.

## GALLIUM Ga, 69·72

**501. Gallium and Its Compounds.**—Gallium is an exceedingly rare element, the richest ores of which rarely contain more than ·02 per cent.; germanite (§ 607) occasionally contains up to *c.* 0·5 per cent. It is found in commercial aluminium in a variable but very small proportion, and also in certain specimens of zinc blende. Its discovery was of particular interest, as Mendeléeff had previously predicted the discovery of an element, 'eka-aluminium,' which would fill the gap then existing in the Periodic table immediately below aluminium. He predicted the properties of this element with remarkable accuracy.

Gallium is a silver-white metal of very low melting point, 30·15° C. The metal remains permanently as a super-cooled liquid at ordinary temperatures if the solid is not brought into contact with it. It is not appreciably volatile even when heated to redness.

In its chemical properties it resembles aluminium, being attacked by both acids and alkalis.

Gallium is unlike aluminium in forming two series of salts, in which it is bivalent and tervalent respectively. The former are strong reducing agents. The latter, which are the usual salts of gallium—if the term usual can be applied to an element so rare—much resemble the salts of aluminium. Thus the chloride, $GaCl_3$, is easily hydrolysed by water, and the sulphate forms alums, such as gallium ammonium alum,

$$(NH_4)_2SO_4.Ga_2(SO_4)_3.24H_2O.$$

## INDIUM In. 114·76

**502. Indium and Its Compounds.**—This element is, like gallium, excessively rare. It is found in the mineral *cylindrite* which contains up to 1 per cent., and also in some zinc blendes.

Indium is a soft white metal of low melting point (155° C.). Its density is 7·28. Its spectrum contains two strong indigo-blue lines, which gave rise to

the name *indium*. It is oxidised at a red heat and burns with a blue flame. It is not attacked by alkalis but dissolves fairly readily in acids.

*Atomic Weight.*—For some time indium was thought to be bivalent on account of its association with zinc. Its equivalent is 38·3, and there was a question whether the metal was divalent with atomic weight 76·6 or tervalent with atomic weight 114. Mendeléeff could only fit indium into the table if it were taken to be tervalent. Evidence drawn from Dulong and Petit's law supported this view and gave a value for the atomic weight of $\frac{6{\cdot}4}{{\cdot}057} = 112$.

Then an indium alum was prepared, showing the element to be tervalent, and finally the vapour density of three different chlorides was determined and the value 114 for the atomic weight was deduced.

Indium forms three series of compounds, in which it is univalent, bivalent and tervalent respectively. In its true salts it is always tervalent. The tervalent sulphate forms alums with univalent sulphates. Indium sulphide is precipitated by the action of hydrogen sulphide on neutral or feebly acid solutions of its salts, therein differing from gallium or aluminium.

## THALLIUM Tl, 204·39

**503. The Element Thallium.**—Thallium is much commoner than gallium or indium, but is none the less only found in a small proportion in the minerals which contain it. It was discovered in the deposits in the lead chambers of sulphuric acid works and was named from the green line in its spectrum (*θαλλός, thallos*, a young shoot). Some difficulty in classifying thallium was at first experienced, for it resembles the alkali metals in some particulars and lead in others. Thallium shows little resemblance, if any, to aluminium, but the Periodic table could not find any space for it other than in this group. Mendeléeff pointed out that to compare thallium (atomic weight 204·0) with aluminium (atomic weight 27·0) was strictly analogous to comparing lead (207·2) with silicon (28), or mercury (200) with magnesium (24), and that no greater likenesses should be expected.

Thallium is obtained from the dust deposited in the flues of the pyrites burners used in the manufacture of sulphuric acid. The separation of thallium from other metals depends on the fact that it is the only metal with a soluble carbonate and an insoluble chloride.

Thallium is a bluish-white metal, soft and malleable like lead. Its melting-point is low, 302° C., and its density is high, 11·85. In these respects thallium has a remarkable resemblance to its neighbour in the Periodic table—lead. Thallium shows a strong green spectral line, and its compounds gives a strong and persistent green colour to the Bunsen flame.

Thallium is oxidised only slowly by dry air at ordinary temperatures, but rapidly when heated. It decomposes water only at a red heat and reacts somewhat slowly with acids. It reacts rapidly with water containing air, giving the hydroxide.

**504. Thallium Compounds.**—Thallium forms two series of compounds, thallous and thallic, in which the element is monovalent and trivalent respectively. The monovalency of thallium and indium in certain of their compounds is due to the peculiar phenomenon of the *inert pair* of electrons. This is discussed in § 588.

*Thallous oxide* $Tl_2O$ is a black powder, which combines with water, forming the hydroxide.

*Thallous hydroxide*, TlOH, is of great interest on account of its resemblance to the hydroxides of the alkali metals. It is made by the action of thallium turnings on water in presence of excess of oxygen,

$$4Tl + O_2 + 2H_2O = 4TlOH.$$

Thallous hydroxide dissolves in water, forming a strongly alkaline solution resembling in most respects a solution of caustic soda or barium hydroxide.

*Thallic oxide* $Tl_2O_3$, is brown in colour. It resembles manganese dioxide or lead peroxide in its properties, giving thallous oxide and oxygen when heated to 800° C., thallous salts and oxygen with concentrated sulphuric acid.

*Thallous salts.*—The monovalent salts of thallium, TlCl, $Tl_2SO_4$, etc., resemble salts of lead or silver rather than of the alkali metals. Thus thallous chloride, bromide and iodide are sparingly soluble in water, as also is the sulphate. Thallous sulphide $Tl_2S$ is black and insoluble like silver sulphide.

*Thallic salts* resemble the compounds of aluminium in some respects. They are, however, not very stable and are oxidising agents. Thallic sulphate does not appear to form true alums but only double salts with alkali metals containing from three to eight molecules of water of crystallisation. There are, on the other hand, true thallous alums, in which the sulphate $Tl_2SO_4$ takes the place usually taken by the sulphate of an alkali metal.

Thallium compounds are poisonous, and the element therein again resembles its neighbours in the Periodic table—mercury and lead.

**504a. Structure of Elements of Group IIIa and Rare-earth Elements,** —Scandium, yttrium, lanthanum, and the rare-earth elements show a most remarkable resemblance. The structures of the rare-earth elements are further discussed in § 510, and, together with those of scandium, yttrium, lanthanum and actinium are given in the table below. It will be seen that the *two* outermost quantum groups are identical in these and in the rare-earth elements, thus accounting for the close resemblance. Scandium, yttrium and lanthanum are often classed as rare-earth elements, but it is better to confine

| Atomic No. | Element. | Electrons of quantum-number | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| 21 | Scandium . | 2 | 8 | 9 | 2 | | |
| 39 | Yttrium . | 2 | 8 | 18 | 9 | 2 | |
| 57 | Lanthanum . | 2 | 8 | 18 | 18 | 9 | 2 |
| 58 | Cerium . . | 2 | 8 | 18 | 18 | 10 | 2 |
| 59 | Praseodymium . | 2 | 8 | 18 | 20 | 9 | 2 |
| 60 | Neodymium . | 2 | 8 | 18 | 21 | 9 | 2 |
| 61 | Promethium . | 2 | 8 | 18 | 22 | 9 | 2 |
| 62 | Samarium . | 2 | 8 | 18 | 23 | 9 | 2 |
| 63 | Europium . | 2 | 8 | 18 | 24 | 9 | 2 |
| 64 | Gadolinium . | 2 | 8 | 18 | 25 | 9 | 2 |
| 65 | Terbium . . | 2 | 8 | 18 | 26 | 9 | 2 |
| 66 | Dysprosium . | 2 | 8 | 18 | 27 | 9 | 2 |
| 67 | Holmium . | 2 | 8 | 18 | 28 | 9 | 2 |
| 68 | Erbium . . | 2 | 8 | 18 | 29 | 9 | 2 |
| 69 | Thulium . . | 2 | 8 | 18 | 30 | 9 | 2 |
| 70 | Ytterbium . | 2 | 8 | 18 | 31 | 9 | 2 |
| 71 | Lutecium . | 2 | 8 | 18 | 32 | 9 | 2 |

this term to the elements from cerium to lutecium in which the 4 quantum group is being filled up to a maximum of 32 electrons.

The table on page 404 shows the relationship of these elements.

## SCANDIUM Sc, 45·1

**505. Scandium and Its Compounds.**—Scandium is found in many minerals, but only in the smallest traces. Some specimens of a mineral called wiikite, containing 1·17 per cent. of scandium oxide, was at one time available, but these are exhausted, and it is extracted from certain specimens of *wolframite*, impure tungsten trioxide, and also from a double silicate of scandium and yttrium, known as *thortvertite*. Scandium forms an oxide, $Sc_2O_3$, resembling alumina but more basic in character. It forms a series of trivalent salts, such as $ScCl_3$, $Sc_2(SO_4)_3$, etc. The sulphate does not form alums. It resembles the rare-earth elements very closely.

## YTTRIUM Y, 88·92

**506. Yttrium and Its Compounds.**—Yttrium is often classed with the rare-earth metals, which it much resembles, although it is definitely not a member of the group of rare-earths, which is now taken to include only those fourteen elements between and including cerium and lutecium (atomic Nos. 58–71). Its properties are not very well known.

The properties of its compounds appear to resemble those of the rare-earths (§§ 509–517) very closely.

## LANTHANUM La, 138·92

**507. Lanthanum and Its Compounds.**—Lanthanum, like yttrium, is associated in nature with the rare-earth metals and resembles them closely. In general, its properties may be taken as those of a typical rare-earth (§§ 509–517).

Lanthanum hydroxide is unusually basic and is slightly soluble in water, being comparable in its basic properties with calcium hydroxide.

## ACTINIUM Ac

**508. Actinium.**—Neither actinium nor its salts have been prepared in a pure state. It is separated from certain radioactive minerals together with any rare-earth compounds present. Its radioactive properties give it a particular interest. It is further treated of in Chapter XXVI.

## THE RARE-EARTH ELEMENTS

**509. The Group of Rare-earth Elements.**—The remarkable group of rare-earth elements comprises, strictly speaking, the fourteen elements appearing between and including cerium and lutecium, viz., the elements cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium.

These rare-earth elements show a most remarkable similarity in chemical properties, a similarity so great that the separation of the pure compounds from the naturally occurring mixtures of rare-earths is one of the most difficult tasks the chemist has to attempt.

**510. Atomic Structure of Rare-earth Elements.**—The peculiarly close resemblance of these elements is due to their all having the two outer layers of electrons, to which most of the chemical properties of an element are to be ascribed, identically the same. The only differences between these ele-

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ments lie in their nuclei, differences in which do not affect chemical properties directly ; and in an inner layer of electrons which is comparatively remote from the part of the atom by which chemical reactions, etc., are influenced. The electronic structures of these elements are given in § 505.

**511. Occurrence.**—The rare-earths occur in a large number of minerals, mostly very uncommon. The most important of these are :—

*Cerite.*—Cerium silicate with the silicates of other rare-earths.

*Monazite.*—Monazite is found in monazite sands, associated with numerous other minerals, and comes for the most part from Brazil, and Travancore in India. It has a commercial value on account of the thorium it contains. Monazite is a mixture of the phosphates of cerium, thorium, lanthanum, yttrium and other rare-earths, iron, aluminium, etc.

Many other rare-earth minerals exist.

**512. Separation of the Rare-earths.**—The process of separating the pure compounds of these rare-earth elements from these complex mixtures is of great difficulty, and a great many ' new elements ' have from time to time been separated and have turned out to be mixtures or to be identical with elements already discovered. *Didymium, mosandrum, phillipium, decipium,*[1] *demonium, lucium, kosmium, neokosmium, glaukodymium, victorium, incognieum, neo-ytterbium, aldebaranium, cassiopeium* and *celtium,* are some of the elements which have been named and afterwards abandoned as mixtures or as elements already known.

The difficulties of the chemist reached their climax when Crookes in 1886 announced that he had examined the spectra given by certain rare-earth compounds when made luminous by bombardment with cathode rays. He had been able to obtain a number of different spectra from the products obtained by fractionating yttrium compounds (cf. § 86), and concluded that yttrium, samarium and gadolinium were made up of some twelve *meta-elements.* It was shown, however, that the varying phosphorescent spectra of this kind were due to small traces of impurity, and the theory was abandoned.

The systematisation of the Periodic table by Moseley's direct determinations of atomic number and Bohr's theories of the atomic structure limited the number of possible rare elements to 14 ; for lanthanum had atomic number 57, and lutecium had atomic number 72, and the other rare-earths lay in the places between these. It may be stated now with reasonable certainty that all the rare-earths are known and are those in the list given in § 505. The discovery of illinium is now regarded as being illusory, but a radioactive isotope obtained by bombardment of neodymium with neutrons or from the fission products of uranium 235, has atomic number 61 and atomic weight 147 and so fills the gap; its half period is 11 days and it cannot be isolated in weighable quantities. It has been named promethium.

It is beyond the scope of this work to discuss the separation of the pure rare-earth elements. The methods used depend on the differences in solubility of certain salts, and on the ease with which certain elements can be precipitated as hydroxides by ammonia, leaving others in solution.

## GENERAL BEHAVIOUR OF THE RARE-EARTHS

The rare-earths are best discussed as a group in a work of this character.

**513. Preparation of the Metals.**—The rare-earth metals may be made

[1] Aptly named from *decipio,* I deceive.

by the alumino-thermic method, by electrolysis of the fused chlorides or by heating the latter with potassium.

An alloy of cerium, lanthanum, praseodymium, neodymium, etc., is made from thorium residues (p. 499) and is known as *mischmetall*. It finds a use in place of aluminium for the preparation of many elements by the reduction of their oxides. The rare-earth metals are for the most part fairly fusible (600–850° C.). They are moderately dense (6–8). They burn vigorously in air or oxygen and are very reactive. They decompose water at 100° C. and are readily attacked by acids.

**514. Hydrides of Rare-earths, $MH_3$.**—The rare-earths combine directly with hydrogen, forming solid hydrides which are comparatively stable.

**515. Oxides of Rare-earth Metals, $M_2O_3$.**—These oxides are the 'earths' themselves. They are made by all the ordinary methods for preparing basic oxides. The oxides are very stable, being reduced to metal with the greatest difficulty.

**516. General Properties of Salts of Rare-earth Metals.**—The salts of the rare-earths, like those of other transition elements, are generally coloured, and the spectrum of light transmitted by them or their solutions shows absorption bands. These absorption spectra are often very complex and, in mixtures, interfere with one another; none the less, they afford a valuable means of distinguishing the rare-earth elements. The flame spectra are peculiar in character and give little assistance. The phosphorescence spectra have been alluded to above and form a valuable means of distinguishing rare-earths. Thus dysprosium gives a yellow band in the spectrum, samarium orange, terbium green, etc.

**517. Hydroxides of Rare-earth Metals, $M(OH)_3$.**—These are precipituted by alkalis from solutions of the corresponding salts. They form gelatinous precipitates. They are more basic than most hydroxides, absorbing carbon dioxide from the air.

**518. Sulphides of Rare-earth Metals, $M_2S_3$.**—Like aluminium sulphide these are decomposed by water and are not formed by the action of hydrogen sulphide on the salts of the metals.

**519. Sulphates of Rare-earth Metals, $M_2(SO_4)_3$.**—These are made by the usual methods. They do not form alums with alkali metals though they form other double salts. The hydrated sulphates are rather sparingly soluble and are remarkable as having retrograde solubility curves.

**520. Nitrates of Rare-earth Metals, $M(NO_3)_3$.**—These are obtained by the usual methods and form readily soluble crystalline hydrates.

They form numerous double salts. Careful heating of the nitrates decomposes some to oxide more easily than others, and this method of separating the rare-earth elements has been found valuable.

**521. Carbonates of Rare-earth Metals, $M_2(CO_3)_3$.**—These carbonates are the only carbonates of tervalent metals which are stable.

**522. Uses of the Rare-earth Elements.**—Cerium oxide is used in gas-mantles (§ 669). Cerium-iron alloys, mischmetall, and other alloys of rare-earth metals are used in the so-called flints of petrol-lighters, etc. Several of the rare-earth compounds have been used for tinting porcelain, and cerium compounds have been used medicinally. The tetravalent ceric compounds are useful oxidising agents.

# CHAPTER XV

## CARBON

**523. Carbon as a Member of Group IV. B.**—Carbon is classed in the Persiodic table with silicon, germanium, tin and lead (*v.* § 586). It bears a greater resemblance to silicon than to any other element, but theresemblance resides rather in the formulæ of the compounds than in a likeness in their properties. To tin and lead carbon bears still less resemblance. Carbon is, in fact, treated by itself, and the study of its compounds forms a separate department of chemistry, known as Organic Chemistry.

The chief points of resemblance between the elements of this group are summarised below :—

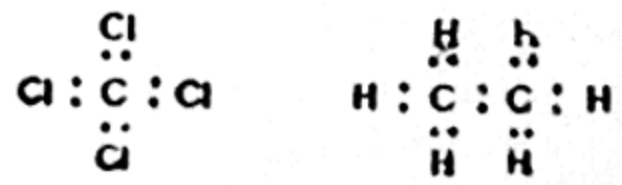
(1) The elements of the group are in certain compounds quadrivalent.

(2) They each form an acidic oxide of the formula $MO_2$.

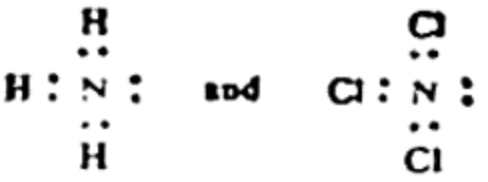
(3) They each form a chloride, $MCl_4$.

The properties of the five elements of Group IV. B show a most interesting and marked gradation of properties as we pass from carbon to lead, but the likeness between the properties of the highest and lowest members is much slighter than is found in the groups which we have already discussed (I.–III.). The properties of the group, as a whole, are further discussed in Chapter XVI.

**524. Unique Position of Carbon among the Elements.**—The extraordinary number, variety and complexity of the carbon compounds, studied under the department of chemistry known as Organic Chemistry, marks this element off from all others. There are three notable reasons for this peculiar behaviour of carbon. In the first place, carbon can form a remarkably strong chemical linkage with itself. Such chains of atoms as —O—O— or S—S—S—, — N = N — are notably unstable, but stable compounds containing chains of carbon atoms up to 60 in number have been made. This allows of the building up of very complex molecules. In the second place, a carbon atom in combination has a fully shared octet of electrons and cannot gain more by co-ordination or any other means. Thus carbon tetrachloride and ethane have no unshared electrons



and therefore are stable substances and less ready to react than others of their class. In contrast are the corresponding compounds of nitrogen, ammonia and nitrogen chloride.



These compounds have pairs of unoccupied electrons and so can readily form molecular or co-ordinate linkages, which are often the prelude to chemical attack. Silicon compounds differ from those of carbon in that silicon has an octet of electrons which can, unlike that of carbon, expand by co-ordination and so form molecular or co-ordinate compounds (cf. § 571).

Finally, carbon forms compounds of about equal stability with a large number of elements, and consequently forms an enormous variety of stable compounds.

**525. Sources of Carbon.**—Pure carbon is found in crystalline form as *diamond* and *bort*, and also as *graphite*. *Coal* contains, but does not consist of, free carbon, as is explained below. In the combined form carbon is found in vast quantities as carbonates; calcium carbonate (*q.v.*, § 365) in particular, forming a considerable part of the earth's crust. The carbon dioxide in the air provides a source of carbon for plants and thus indirectly for animals. Finally, organic matter of all kinds and the products of plants and animals in general contain carbon. Mineral oil, asphalt and bitumen, which may be the products of animal or plant life in past ages, also contain a high percentage of this element.

**526. Allotropy of Carbon.**—Carbon exists in two allotropic forms—

(*a*) Diamond.

(*b*) Graphite.

Until recent years a third form, amorphous carbon, was included. Some authors have taken the view that there is a truly amorphous carbon and that coke, charcoal, lamp-black, etc., are mixtures of this with more or less graphite; but recent researches indicate that the varieties of carbon (coke, lamp-black, charcoal, etc.) included under that heading, differ only from graphite in their purity, their size and shape of the particles and their porosity. Their intimate structure as revealed by X-ray methods definitely shows their identity with graphite. The peculiar properties of the several varieties of "amorphous carbon" are apparently due to surface effects and to the presence of hydrocarbon impurities. Diamond and graphite, moreover, are the only forms of carbon with definite, fixed and invariable properties.

The two definite allotropes, diamond and graphite, will co-exist

indefinitely without change, but it appears that graphite is the stable form below 1,100° C., and below 8,000 atmospheres pressure.

Thus diamond becomes converted into graphite when heated at ordinary pressures, and carbon when deposited from a solvent, such as melted iron, is deposited at ordinary pressures as graphite. The heats of combustion of the two forms indicate that graphite is the stable form, for its heat of combustion (94·27 cal./gm. atom) is less than that of diamond (94·43 cal./gm. atom). Graphite has therefore less chemical energy and is the more stable form.

**527. The Diamond.**—The diamond, most famous and valuable of gems, owes its popularity to its hardness and its high dispersion and refractive index, properties which render it imperishable and lustrous. Its rarity and the guarantee of wealth provided by its possession adds to its desirability. In the past diamonds have been exceedingly rare, but to-day the high price of the gems is due to the strenuous efforts of the mining companies to restrict output. Quite apart from its beauty, the diamond has industrial uses, in particular for the manufacture of diamond drills for rock-boring, which may cost £2,000 each, and for such purposes as glass-cutting, gem engraving, wire-drawing, etc.

Diamonds are found in alluvial deposits, as in Brazil, but their chief source is in the so-called 'pipes' of South Africa. These 'pipes' are apparently the shafts of ancient volcanoes, and are filled with a peculiar type of rock, known as 'blue ground.' This is hard when excavated, but when left to weather, falls to powder. The diamonds are separated first by hand-picking and then by washing the clayey weathered blue ground over boards coated with grease. The diamonds adhere to the grease, and the clay, etc., passes on with the water. Artificial diamonds have proved unexpectedly difficult to make. Crystals of an element may be made, as a rule, by deposition from a solution (cf. sulphur), by gradual freezing of the melted element or by sublimation. Carbon has only recently been melted, and it solidifies to pure graphite and not diamond. At very high temperatures it sublimes below its melting point. The vapour of carbon, moreover, condenses as 'amorphous carbon,' and not as diamond. Carbon does not dissolve in any of the usual solvents, but it is found to dissolve to an appreciable extent in molten iron, which when cooled normally deposits graphite only. The occurrence of diamonds in volcanic shafts suggested the idea that, if the carbon were deposited from molten iron under high enough conditions of temperature and pressure, diamond would be formed instead of graphite. There appears to be evidence that the catalytic agency of iron is necessary for its formation and that heat and pressure alone do not suffice.

Moissan, in 1896, was the first to prepare artificial diamonds. Moissan placed pure iron and sugar charcoal in a carbon crucible, which fitted into a recess in the large electric arc furnace shown in Fig. 98. The iron was heated in the flame of the arc until it boiled violently, reaching a temperature of about 2,000° C., and at this high temperature it dissolved a good deal of carbon. The crucible and boiling iron were then taken out and plunged into cold water or, better, into melted lead—a far better conductor of heat. The rapid cooling solidified a surface skin of iron and the contraction of this exerted an intense pressure on the melted iron within. The carbon crystallising under these conditions assumed the form of minute diamonds (Fig. 99), which were recovered by dissolving away the iron with an acid. The diamonds in no case exceeded ¾ mm. in length.

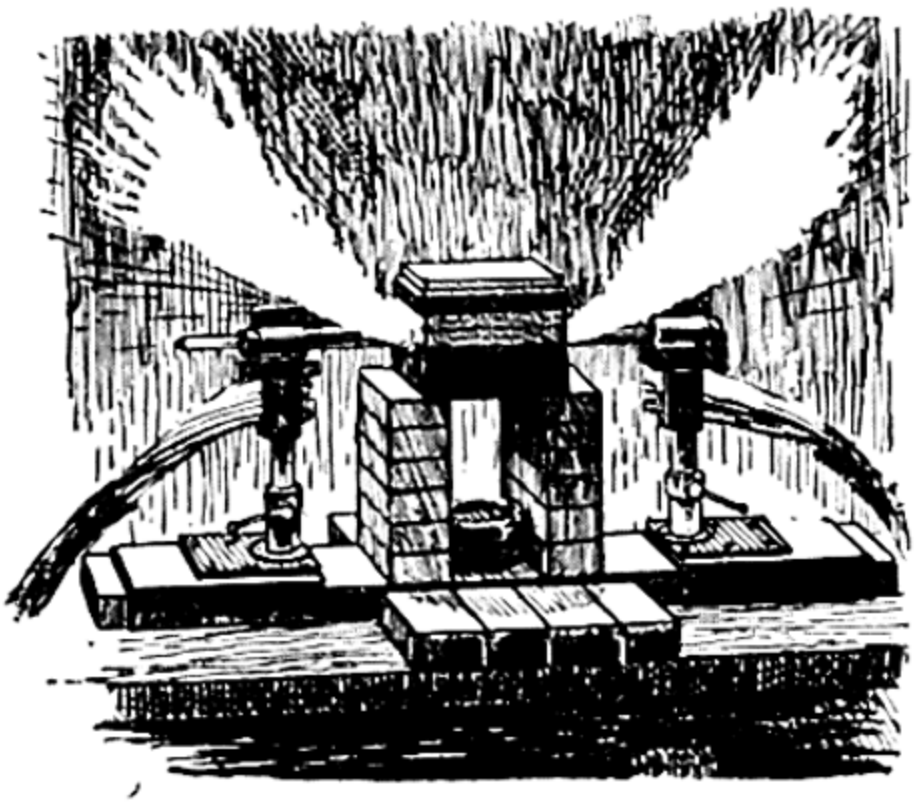


Fig. 98.—M. Moissan's electric furnace.

The diamond forms transparent crystals of octahedral form. Simple octahedra are rare, for the usual figure is one derived from the octahedron and has either twenty-four or forty-eight faces (Fig. 39), which shape makes the native diamond look very like a rounded pebble. The edges of the crystals are curved. The diamond is the hardest substance known. The refractive index of diamond (2·417) is considerably higher than that of any other solid,[1] and to this its resplendent lustre is to be attributed, while its high colour-dispersion gives it 'fire.' The numerous total reflections in the interior of the gem bring about the play of light which characterises it. The internal structure of the diamond has been investigated and it appears that the carbon atoms of which it is composed are chemically combined into a 'giant molecule' (§ 529a). This theory helps to account for its high density (3·3–3·5) and its chemical inertness.

Fig. 99.—Diamonds obtained by Moissan, magnified thirty-three times.

The diamond is very resistant to chemical action. It burns, though with great difficulty and at a high temperature, forming carbon dioxide and leaving behind an almost negligible ash of mineral matter. The only chemical reagents which attack the diamond at

[1] Glasses have refractive index *c.* 1·4–1·7.

the usual laboratory temperatures are fused sodium and potassium carbonates, which slowly convert it into carbon monoxide.

*Varieties of Diamond.*—Diamond occurs associated with some graphite in the form of *carbonado* or *bort*. This mineral has the intense hardness of diamond, but presents a black and lustrous appearance. It can be used as a substitute for diamond in drills, etc. It has recently been shown that two modifications of diamond exist, differing slightly in physical properties.

**528. Graphite.**—Graphite is found native in Siberia, Ceylon and the U.S.A.

Graphite is made by subjecting amorphous carbon to intense heat. In the Acheson graphite furnace (Fig. 100) a rectangular fire-brick casing of considerable size is lined with coke dust, within which are packed either masses of coke or articles formed of amorphous carbon which it is desired to convert into graphite. Large carbon electrodes are inserted in each end of the furnace and a current is passed sufficient to raise the contents of the furnace to a white heat. When the mass is allowed to cool, the amorphous carbon is found to be converted into graphite.

Graphite is a dark grey substance of characteristic greasy feel and lustre. Its density is 2·1–2·3. It crystallises in hexagonal plates, but

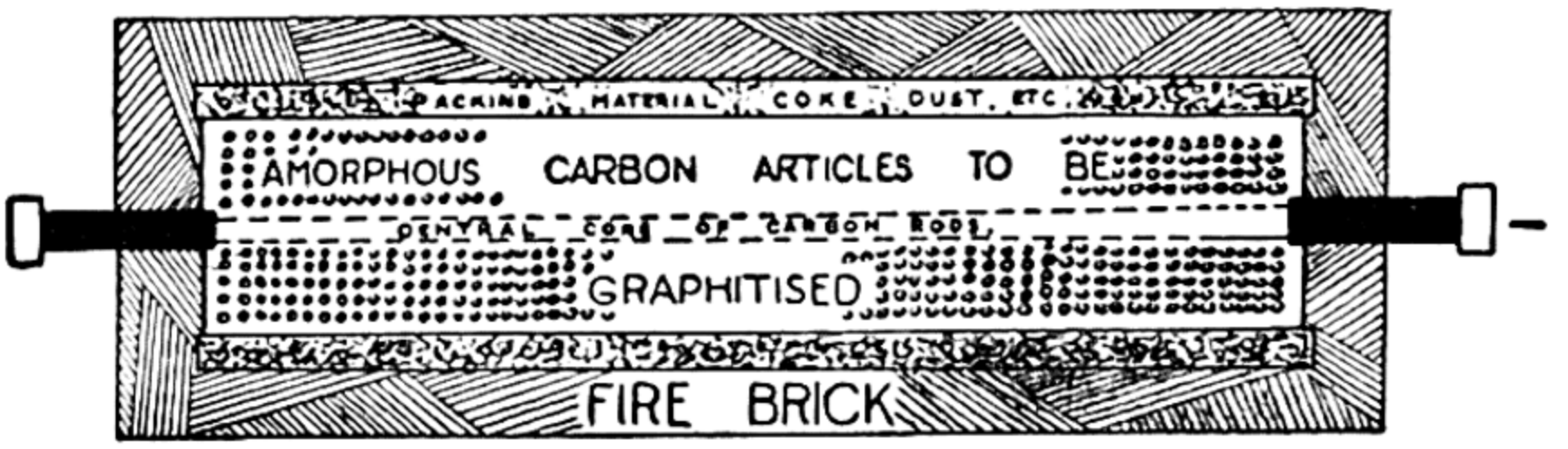



FIG. 100.—Acheson graphite furnace (plan).

commonly has a foliated structure somewhat like that of mica. Graphite is soft and an excellent lubricant, and from these properties its chief uses arise. The centres of 'lead' pencils are commonly composed of a mixture of graphite and clay. Graphite is used as a lubricant, mixed with various greases.

Graphite is a fairly good conductor of electricity; electrical apparatus is often composed of carbon 'graphitised' by heating it to a high temperature out of contact with air. Powdered graphite, 'black lead,' is rubbed on plaster casts, etc., to make them sufficiently good conductors of electricity to be electroplated. Graphite is widely used for the brushes of small dynamos, since it is a good conductor and soft enough to shape itself to fit the revolving commutator. The electrodes used in electrolytic chemical processes

are usually of graphite, the only cheap substance which is at once a good conductor and chemically inert.

Graphite is chemically very inert, but not to the same extent as the diamond. It can be made to burn when heated to a high temperature, though only very slowly, and its resistance to heat causes it to be used, together with fireclay, in making crucibles. It is not attacked at temperatures below 100° C., except by a mixture of potassium chlorate and nitric acid, which oxidises it to a peculiar compound—graphitic acid. At higher temperatures any reagent which liberates oxygen will attack it. Thus graphite is oxidised when heated with potassium nitrate, potassium chlorate, etc.

**529. Varieties of Graphite. 'Amorphous' Carbon.**—The term amorphous carbon is applied to a large number of materials, consisting of more or less pure carbon and not of any crystalline form visible to the naked eye, aided by the microscope. These varieties consist of impure graphite, as has been shown by X-ray examination of their intimate structure. They include charcoal, lamp-black, soot and coke, and coal is also usually considered to contain amorphous carbon.

**529a. Structures of Diamonds, Graphite and Charcoal.**—The X-ray examination of these forms has enabled us to map out their structure with great certainty.

Diamond has its atoms arranged in a series of interlacing hexagons Every carbon atom is joined by a chemical linkage to four others.

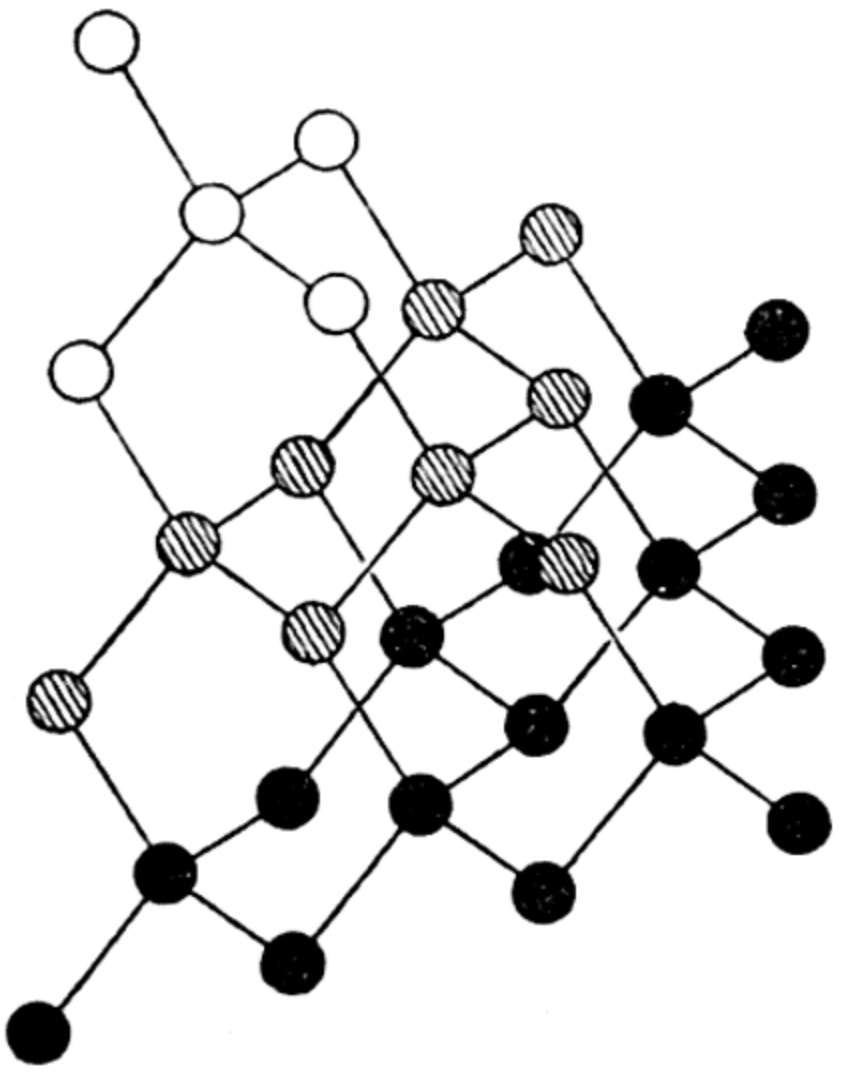


Fig. 101.—Structure of diamond.

Thus, to volatilise, dissolve or attack diamond chemically, it is necessary to break the strong covalent linkages holding its atoms together. This accounts for its hardness; and the intimate associa-

tion of the atoms (which share each other's electrons) accounts for their nearness and the consequent high density of the solid. The distance between the adjacent atoms is $1{\cdot}54 \times 10^{-8}$ cm., which is the same as that between the adjacent carbon atoms in aliphatic compounds.

Graphite on the other hand consists of sheets of carbon atoms joined by covalent linkages into planes.

The individual planes are not, however, chemically linked as shown by their distance from each other. The carbon atoms in each plane are $1{\cdot}42 \times 10^{-8}$ cm. apart, the same distance as the carbon atoms in benzene and other aromatic compounds: the individual planes however are about $3{\cdot}41 \times 10^{-8}$ cm. apart. Graphite is therefore readily cleaved along the line of the planes which are themselves not readily split up, hence its foliaceous structure, softness and lubricating power. It is more readily attacked than diamond, because the edges of the planes are open to chemical attack.

Charcoal and other forms of 'amorphous' carbon appear to have the graphite structure, but with the planes of carbon hexagons smaller and more irregularly disposed. They have therefore many more "edge" atoms linked only to two others and are more reactive than graphite. Chemical evidence (§ 530) as well as X-ray examination reveals the hexagonal arrangement.

**530. Charcoal** is perhaps the typical form of 'amorphous' carbon Charcoal is produced when organic matter is heated to a high enough temperature to decompose it into volatile compounds and a residue containing carbon and any mineral matter contained in the original substance. Very pure amorphous carbon may be made by heating sugar in this way. Steam and various tarry products, furfural, etc., are evolved and a black residue left. This carbon is then heated in a current of chlorine to remove traces of hydrogen. It is exceedingly difficult to remove the last traces of hydrogen, oxygen and moisture. The action of magnesium on carbon tetraiodide (dissolved in carbon disulphide) yields a very pure form of amorphous carbon, $CI_4 + 2Mg = C + 2MgI_2$.

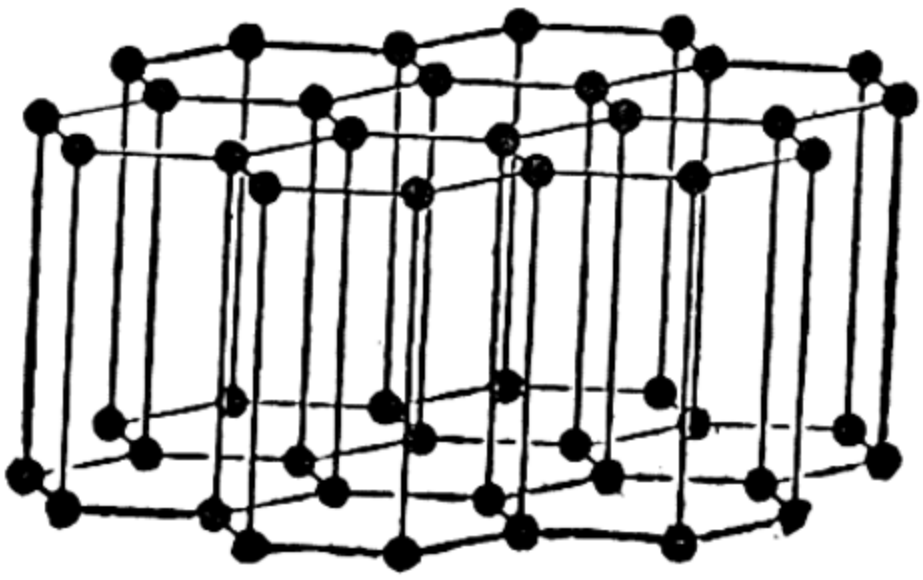


FIG. 102.—Structure of graphite.

Ordinary charcoal is prepared by heating wood in the absence of sufficient air for its combustion. The simplest method of doing this on the large scale is to build a heap of logs radiating from a central shaft and to cover this with turf. The heap is lighted through one

of the air holes at the base ; and by regulating the air supply, the heap is converted into charcoal with as little waste of wood as possible. The vapours evolved when wood is heated contain valuable products, notably acetic acid, acetone and methyl alcohol, and the distillation of wood is to-day a considerable industry. The wood is heated in retorts of various patterns, and the residue, after the distillation, consists of charcoal. The supply so obtained exceeds the demand and much of the charcoal is burned as fuel wherewith to distil more wood.

Charcoal is a black porous substance of very low apparent specific gravity (0·2 to 0·9), though the true density approximates to that of graphite. Since charcoal is very porous it has an enormous area of surface and exhibits surface effects in a remarkable degree. All substances retain a film of gas upon their surfaces, but the amount of gas so retained is very small. Charcoal, having an enormous surface, absorbs gases in a remarkable manner. Coconut-shell charcoal and that derived from very hard woods are peculiarly active. A piece of freshly prepared coconut charcoal will absorb 176 times its volume of ammonia gas (at N.T.P.), 71 times its volume of carbon dioxide, and considerable proportions of other gases. The modern activated charcoals have even greater absorptive power. The gases are evolved once more on heating. If the charcoal is cooled in liquid air it becomes still more efficient, and charcoal so cooled is used in the production of very high vacua.

The absorption of gases by charcoal is made use of in gas-masks. Ordinary charcoal adsorbs no great quantity of gas, probably because it has already adsorbed various hydrocarbons. Charcoal for adsorption is *activated* by heating it to 800°–1,000° C. in a current of steam, so decomposing or removing these hydrocarbons.

In a similar fashion charcoal will *adsorb* substances from solution. *Animal charcoal* derived from bones is very efficient ; this charcoal consists of amorphous carbon mixed with the calcium phosphate of the bones in such a way as to expose a very large surface. If animal charcoal be boiled with a solution of litmus, port wine, tea or other liquid coloured by a complex organic substance, the liquid is decolorised, the dye being adsorbed by the charcoal. The process is enormously used in the decolorising of sugar-cane juice in the making of white sugar.

Charcoal is the most reactive of the forms of carbon, and its activity is probably due to its enormous surface. It burns readily to carbon dioxide,

$$C + O_2 = CO_2,$$

some carbon monoxide (*q.v.*) being formed if the supply of air be

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deficient. It is a useful fuel in that it will smoulder for long periods under the coating of white ash it forms, and can, at a minute's notice, be fanned to a bright glow.

Charcoal reacts with many oxidising agents. With nitric acid it forms carbon dioxide, water and nitrogen peroxide,

$$C + 4HNO_3 = 2H_2O + 4NO_2 + CO_2.$$

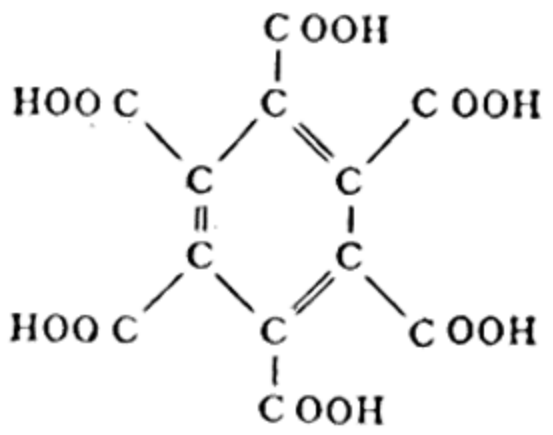
With sulphuric acid carbon dioxide and sulphur dioxide and water result,

$$C + 2H_2SO_4 = CO_2 + 2H_2O + 2SO_2.$$

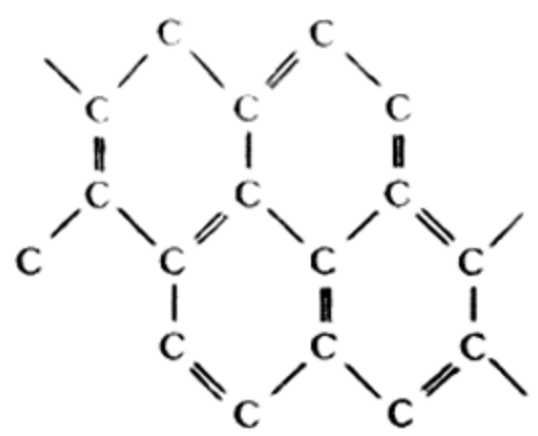
A curious side reaction is of interest. When charcoal reacts with sulphuric acid a small proportion of mellitic acid, $C_6(COOH)_6$, is formed at the same time as the carbon dioxide and sulphur dioxide,

$$12C + 9H_2SO_4 = C_6(COOH)_6 + 6H_2O + 9SO_2.$$

Mellitic acid has the structure,



and accordingly it appears probable that the carbon atoms in charcoal are combined into some such structure as



Charcoal is a useful reducing agent at high temperatures. The oxides of most metals, heated with charcoal, are reduced to the metal with formation of carbon monoxide or dioxide,

$$2CuO + C = 2Cu + CO_2$$
$$Fe_2O_3 + 3C = 2Fe + 3CO.$$

This is the primitive process for smelting metallic ores. Oxysalts, such as nitrates and sulphates, are reduced when heated with charcoal, the former with incandescence, the latter less easily. Thus barium sulphate heated strongly with charcoal is reduced to the sulphide

$$BaSO_4 + 4C = BaS + 4CO.$$

**531. Lamp-black** is a finely divided form of amorphous carbon. It is made by burning various oils, such as creosote or petroleum, and collecting the soot produced on blankets suspended in the smoke.

It forms a fine black impalpable powder, containing a certain amount of greasy matter derived from the oil. It is used as a black pigment for paints, india ink, etc.

*Carbon-black* or *gas-black* is made in vast quantities by burning natural gas (§ 537). It is used as a filler for rubber which in the finished state may contain 40 per cent of gas-black.

**532. Soot.**—Soot is similar to lamp-black but contains also a good deal of mineral matter from the ash of coal and also tarry products and ammonium salts. It is the latter two substances that render it useful to gardeners as an insecticide and fertiliser, the carbon being inert.

**533. Coal.**—"Ordinary coal is a compact, stratified mass of 'mummified' plants (which have in part suffered arrested decay to varying degrees of completeness), free from all save a very low percentage of other matter."

This definition applies to all types of coal, but 'cannel coal' contains also remains of minute animals, fish, etc. The source of the great coal-fields is the vegetable remains of great swamps, probably formed by the blockage of sluggish watercourses by vegetation, or more rarely, by the *débris* of primæval forests carried down by rivers and deposited in deltas. Minor seams may have been formed in many other ways, from peat deposits, accumulations of dead leaves in primæval forests, etc.

That vegetable matter was the original source of coal has long been obvious from the common occurrence of fossil leaves, tree trunks, etc., in the mineral, while careful examination of coal with the microscope shows that coal is almost completely composed of plant remains in various stages of decomposition.

At one time coal was regarded as a 'form of carbon,' but in fact it only contains a small proportion of *free* carbon. That this is the case is clear on several grounds :—

(1) Coal is partly soluble (up to 30 to 40 per cent.) in pyridine and to a lesser extent in other solvents, while carbon is completely insoluble.

(2) Coal yields a variety of volatile products when heated. These amount to some 30 per cent. of its weight.

(3) Coal always contains a small percentage of combined hydrogen. This amounts only to a few units per cent., but owing to the low atomic weight of hydrogen, this represents enough to form a high percentage of complex hydrocarbons and other organic compounds. Thus the white solid hydrocarbon anthracene contains only about 6 per cent. of hydrogen, while coal often contains as much as 5 per cent. of the element.

(4) Coal is not homogeneous. Very thin sections of coal show

bands of transparent yellowish and brownish materials interspersed with blackish bands and granules.

Coals of many different types are distinguished. The chief of these are described below.

*Lignite or brown coal* is a material intermediate in character between peat and coal. It is very moist as mined and is of poor heating power. Extensive deposits exist in Germany and the U.S.A., but not in this country.

*Bituminous coal* is the commonest type of coal. It provides a large proportion of gas when heated and burns with a bright and long flame. The peculiar *cannel coal* is of this type. Some of the cannel coals consist almost wholly of spores and are so rich in hydrogen compounds that when ignited they will burn like a candle (whence its name).

*Anthracite* is a very hard coal, containing but a small proportion of volatile compounds. It burns without flame and produces little ash.

Analyses of typical specimens of these coals are given below. Naturally there are considerable variations in specimens from different sources.

| | C | H | O | N | S | Ash. |
|---|---|---|---|---|---|---|
| Lignite (dry) . | 60–75 | 5 | 20–35 | 0·5–1·5 | — | 5–15 |
| Bituminous coal . | 75–90 | 4·5–5·5 | 5–20 | 1·5 | 0·9 | 7 |
| Anthracite . . | 90–93 | 3 | 2–3 | 0·5–1·5 | 0·7 | 3 |

The analyses of varieties of coal given above show that as coal becomes less like the original vegetable matter, the proportion of hydrogen in it diminishes and the proportion of carbon increases.

The action of heat upon coal is discussed under the heading of coal gas (pp. 426–431).

**534. Coke** is the solid product of the action of heat upon coal. It consists of a porous mass of carbon containing very little hydrogen, but retaining all the ash of the coal from which it was derived.

Typical coke contains :—

| | |
|---|---|
| Carbon . . . . . | 85–90 per cent. |
| Volatile matter . . . . | 0·5–2 „ |
| Ash . . . . . | 8–11 „ |

It is much used in large scale chemical operations, such as smelting, on account of its cheapness.

**535. Atomic Weight of Carbon.**—That carbon has an atomic weight of *c.* 12 is shown by the fact that there are never less than 12 gms. of carbon in a gram-molecule of any of the organic compounds (many thousands in number) of which the molecular weight has been determined (*v.* § 62). Dulong and Petit's law gives anomalous results at ordinary temperatures, as in the case of several other elements of low atomic weight.

The exact determination of the atomic weight of carbon has been made by the chief methods.

(1) Numerous investigators have burned a known weight of diamond or graphite to carbon dioxide in a current of oxygen and found the weight of the carbon dioxide (absorbed in potash as in an organic combustion analysis).

(2) An entirely different method was employed in 1915. Richards and Hoover neutralised an exactly known weight of sodium carbonate of the highest purity with hydrobromic acid, forming sodium bromide, and precipitated and weighed the silver bromide obtained by addition of silver nitrate to the sodium bromide. They thus obtained the ratio $Na_2CO_3$ : Ag, and the value 12·003 was the mean value obtained.

(3) A method similar to the above, but using benzoyl chloride $C_6H_5.COCl$ has been employed and has the advantage that the atomic weight of sodium is not involved.

(4) The atomic weight of carbon has been found by determining the density of carbon monoxide, methane, etc., with great exactness.

The most probable value for the atomic weight of carbon is 12·01.

There are two isotopes $^{12}C$ and $^{13}C$. The latter has been isolated in considerable quantity by diffusion methods and finds a use as an indicator.

**536. Hydrides of Carbon.**—The compounds of hydrogen and carbon number thousands, for almost every one of the simpler compounds of these elements for which a formula can be written is capable of realization. These hydrocarbons are studied in Organic Chemistry, and it is our purpose here to study only three typical hydrocarbons, viz. :—

| | |
|---|---|
| Methane . . . . . | $CH_4$ |
| Ethylene . . . . . | $C_2H_4$ |
| Acetylene . . . . . | $C_2H_2$ |

**537. Methane $CH_4$. Occurrence.**—The gas, methane, occurs naturally as a constituent of 'natural gas' and 'firedamp,' and is also evolved from decomposing vegetable matter in ponds and marshes.

Natural gas is associated with oil-deposits. Mineral oil is commonly found in a geological formation consisting of an impervious dome which encloses a space containing gas, oil and water. The former is at high pressure and drives out the oil from a boring with great force. Natural gas is widely employed in the United States, where, in many districts, it is possible to supply it to towns, which receive their fuel for lighting and power merely for the very low cost of collecting the gas. Natural gas is rapidly replacing coal-gas over wide areas, as methods of pumping it long distances are perfected.

The decomposition of vegetable matter by certain bacteria produces methane. If the bottom of a pond be stirred with a stick

gas bubbles often rise to the surface, and if these are collected in an inverted vessel they are found to burn with a pale flame and, in fact, to consist of methane.

*Firedamp.*—Coal has been produced by the decomposition of vegetation under moist conditions, and it is commonly found to contain cavities which enclose methane under pressure. When certain types of coal are mined, the methane or 'firedamp' may be heard to 'sing' or whistle as it escapes from cracks in the coal. Since a mixture of 5 per cent. of methane with air is explosive the use of naked lights in coal mines where much methane is found, at one time caused many fatal explosions. The invention of the safety lamp by Sir Humphry Davy was the means of preventing many of these. In the safety lamp the flame which provides the light is isolated from the surrounding atmosphere by copper gauze. The cooling effect of the copper is such that the flame of methane cannot traverse it and even if the methane burns within the lamp the flame cannot spread to the surrounding air.

If methane is present the flame of the lamp becomes enlarged and a detector for methane is based on this principle. It consists of a safety-lamp containing a small oil flame which grows bigger in a methane-containing atmosphere by reason of the combustion of the methane-air mixture, which, though too dilute to burn alone, forms a pale mantle of flame about the oil flame which keeps it burning.

Methane is an important constituent of coal gas (*q.v.*).

**538. Preparation of Methane.**—Methane is made by three chief methods :—

(1) The simplest is the action of water on aluminium carbide—now an article of commerce.

$$Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3.$$

The gas may be purified by passing it through potassium permanganate solution to remove acetylene, etc., and then dried with sulphuric acid.

(2) The action of alkalis upon an acetate furnishes methane. Equal weights of soda-lime and anhydrous (fused) sodium acetate are ground together and the mixture is heated in a hard glass test tube or, better, an iron retort or copper flask. The methane may be purified as above and, if so required, collected over water,

$$\begin{array}{l|l} CH_3 & .COONa \\ +H & ONa. \end{array} = CH_4 + Na_2CO_3.$$

(3) Methane is formed by the action of the zinc-copper couple on methyl iodide $CH_3I$. The zinc-copper couple acts as a source of nascent hydrogen.

$$CH_3I + 2H = CH_4 + HI.$$

**539. Formulæ of Hydrocarbon Gases.**—The formula of methane, or indeed any other gaseous hydrocarbon, may be obtained by exploding a mixture of the gas with oxygen in a eudiometer (*v.* Fig. 67). Water and carbon dioxide are produced. The former condenses and causes a contraction of the gases on cooling, equal in extent to the volume of steam produced by the combustion. The carbon dioxide may then be completely absorbed by the addition of a little strong caustic potash solution through a bent pipette.

Suppose that $n$ c.c. of the hydrocarbon are mixed with a large excess of oxygen and exploded. Let a diminution of $m$ c.c. be found to have taken place when the gases have cooled to their former temperature, and on adding potash let a further diminution of $p$ c.c. result. We require the formula of the hydrocarbon.

Let the formula of the hydrocarbon be $C_aH_b$,

Then $$C_aH_b + \left(a + \frac{b}{4}\right)O_2 = a\,CO_2 + \frac{b}{2}H_2O$$

1 vol. $a + \frac{b}{4}$ vols. $a$ vols. $\frac{b}{2}$ vols.

1 c.c. of the hydrocarbon disappears together with $a + \frac{b}{4}$ c.c. of oxygen and in its place appear $a$ c.c. carbon dioxide; the water condenses and its volume is negligible. On adding potash the carbon dioxide ($a$ c.c.) is absorbed.

$\therefore$ For every $n$ c.c. hydrocarbon there is a diminution of $n + \left(a + \frac{b}{4}\right)n - an$ c.c., and a further contraction on adding potash of $an$ c.c.

$$\therefore\ m = n\left(1 + \frac{b}{4}\right) \text{ and } p = an.$$

$$\therefore\ a = \frac{p}{n} \text{ and } b = 4\left(\frac{m}{n} - 1\right).$$

The formula is therefore $C_{\frac{p}{n}}H_4\left(\frac{m}{n} - 1\right)$, and by substituting actual experimental figures for $n$, $m$, and $p$, any such formula may be found.

Methane is in this way proved to have the formula $CH_4$.

*Physical Properties.*—Methane is a colourless gas, without taste or smell. It is lighter than air, its density being 8 ($H_2 = 1$). Methane is only slightly soluble in water (3·7 vols. per 100 vols. water at 15° C.), and is liquefied and solidified with difficulty (B.P. — 164° C., F.P. — 184° C.).

*Chemical Properties.*—Pure methane burns with a pale and almost non-luminous flame, forming carbon dioxide and water,

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

Mixtures of air and methane are explosive when as little as 5 to 6 per cent. of methane is present.

Methane is a remarkably stable substance, being attacked by very few reagents, and therein is in contrast to most hydrogen compounds. Chlorine attacks it, a mixture of the two gases burning to form hydrogen chloride and carbon,

$$CH_4 + 2Cl_2 = C + 4HCl.$$

If a mixture of chlorine and methane is exposed to sunlight various *substituted* compounds are formed. The formation of these should be contrasted with the *additive* compounds formed by ethylene and chlorine (§ 543).

$$\begin{aligned} CH_4 + Cl_2 &= CH_3Cl + HCl \\ CH_3Cl + Cl_2 &= CH_2Cl_2 + HCl \\ CH_2Cl_2 + Cl_2 &= CHCl_3 + HCl \\ CHCl_3 + Cl_2 &= CCl_4 + HCl \end{aligned}$$

The substances formed are known as methyl chloride, methylene chloride, chloroform and carbon tetrachloride, or as mono-, di-, tri- and tetra-chloromethane.

Methane is unattacked by other chemical reagents, and it is this remarkable inertness which has given to the group of hydrocarbons, of which it is the chief representative, the name of *paraffins*—a name derived from the Latin *parum affinis*, of little affinity.

**540. Ethylene $C_2H_4$. Occurrence and Preparation.**—Ethylene is contained in natural gas (§ 537), of which, however, it forms but a very small proportion.

Ethylene is prepared, as a rule, by the action of sulphuric acid on alcohol. The reactions involved are the formation and subsequent decomposition of ethyl hydrogen sulphate.

$$\begin{aligned} C_2H_5OH + H_2SO_4 &= C_2H_5.HSO_4 + H_2O \\ C_2H_5.HSO_4 &= C_2H_4 + H_2SO_4, \end{aligned}$$

or summarising,

$$C_2H_5OH = C_2H_4 + H_2O.$$

Thirty cubic centimetres of alcohol are mixed with 100 c.c. concentrated sulphuric acid in a 2-litre flask and 25 gms. of anhydrous aluminium sulphate are added. This latter substance tends to prevent the frothing which otherwise is troublesome. On heating to

160° C. on a sand bath, ethylene is formed, together with a good deal of sulphur dioxide, ether vapour, etc. Further gas is obtained by adding a mixture of equal volumes of alcohol and sulphuric acid

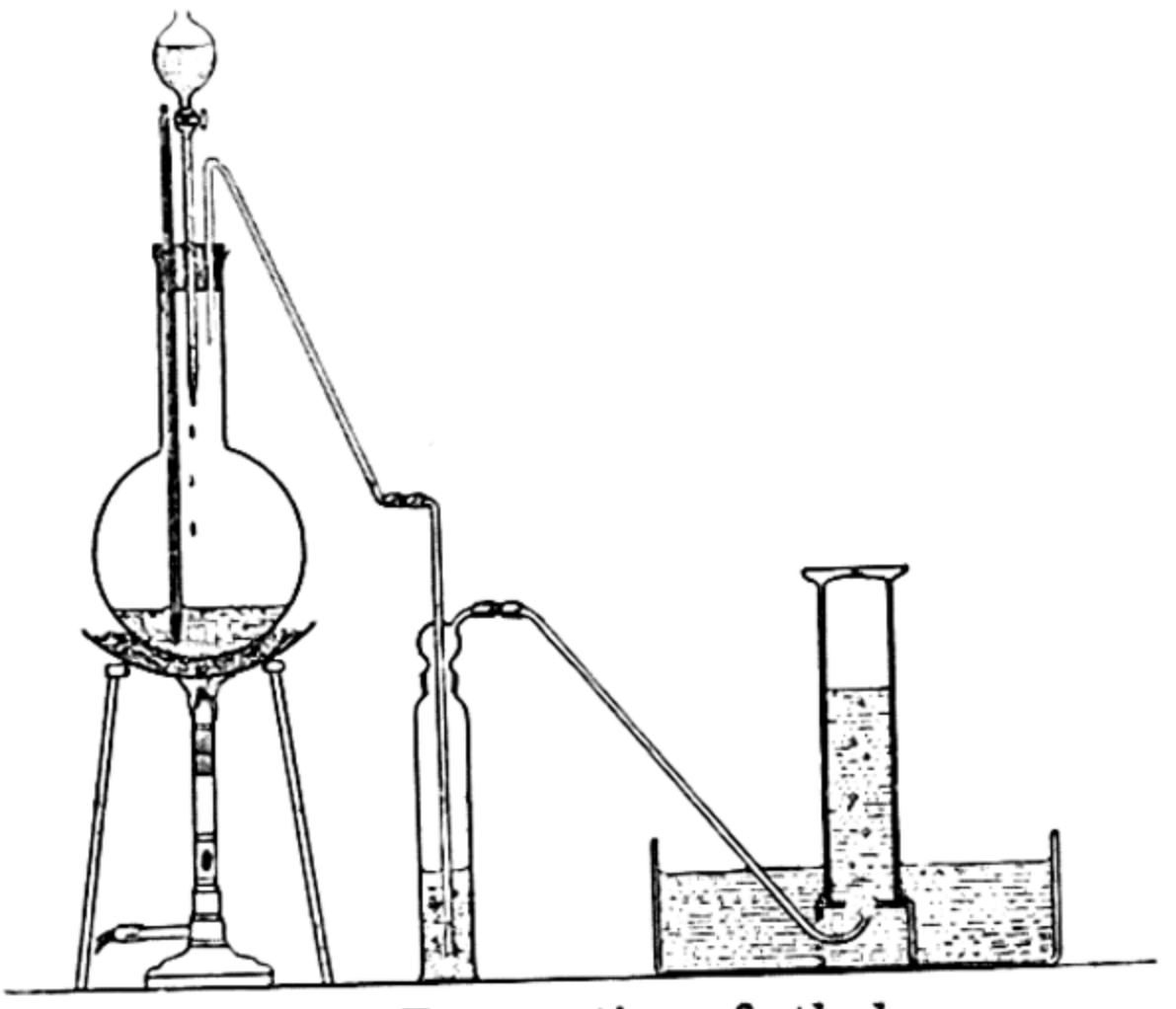


FIG. 103.—Preparation of ethylene.

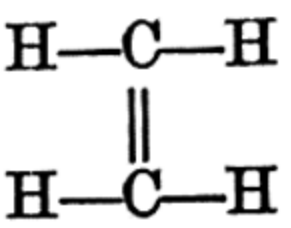
from a dropping funnel. The gas may be purified by passage through strong potash and then may be collected over water.

A much purer gas is produced by dropping alcohol into phosphoric acid heated to 250° C. The reaction is, however, somewhat troublesome to control. On the large scale, alcohol vapour is passed over heated phosphorus pentoxide.

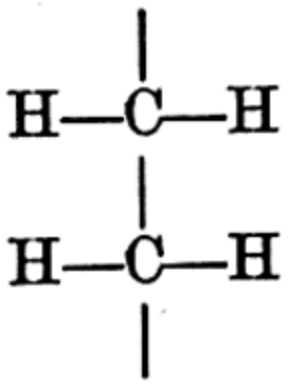
**541. Physical Properties of Ethylene.**—Ethylene is a colourless gas with a faint sweetish smell. It has recently been used as an anæsthetic in medical practice. The gas is of almost the same density as air (D = 14, $H_2 = 1$). It liquefies at — 102·7° C. under normal pressure. Ethylene is sparingly soluble in water.

**542. Formula and Structure.**—The methods described in § 539 show its formula to be $C_2H_4$. But since carbon is tetravalent we can only write this formula by assuming a *double linkage* to exist, as in formula A.

A.

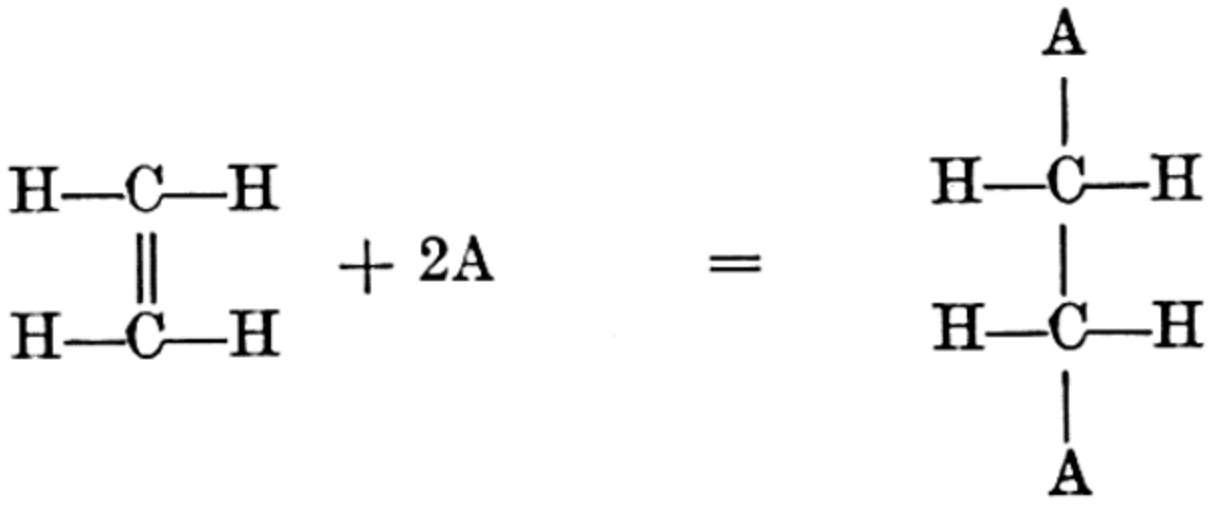


B.



There is a good deal of evidence that formula A represents its chemical behaviour more closely than does formula B, though most

of this evidence belongs to the domain of organic chemistry. The physical meaning of the double bond is, presumably, that the two carbon atoms are linked by means of four electrons in place of the usual two. A linkage of this type may be regarded as being stronger than a single bond, but not twice as strong. It appears to involve a condition of strain in the molecule and is therefore comparatively unstable and easily altered. Accordingly, we find that ethylene readily forms *addition products* as represented by the following general equation :—



**543. Chemical Properties of Ethylene.**—Ethylene burns with a bright smoky flame, forming carbon dioxide and water,

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O.$$

It forms addition products with chlorine and bromine

$$C_2H_4 + Cl_2 = C_2H_4Cl_2$$
$$C_2H_4 + Br_2 = C_2H_4Br_2.$$

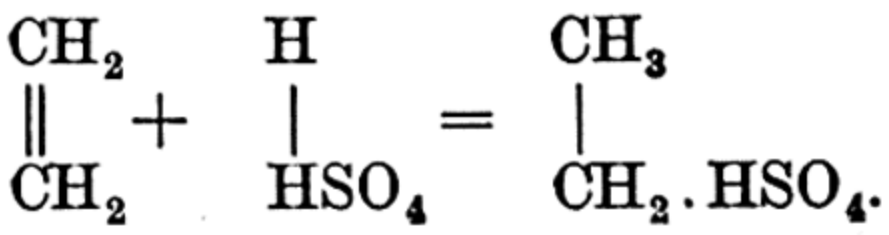
The substance formed with chlorine is termed ethylene dichloride and is an oil. One of the first properties noticed about ethylene was the fact that with chlorine it produced an ‘ oil ’—hence its former name, *olefiant gas*. With hydrobromic acid ethyl bromide results,

$$C_2H_4 + HBr = C_2H_5Br.$$

Oxidising agents, such as potassium permanganate, convert ethylene into glycol,

$$C_2H_4 + H_2O + O = C_2H_4(OH)_2.$$

Fuming sulphuric acid absorbs ethylene, converting it into ethyl hydrogen sulphate,



Ethylene then is a highly reactive substance, tending to form addition products, and is in strong contrast to methane, which is unreactive and tends to form substitution products.

**544. Acetylene $C_2H_2$.**—The gas acetylene is readily prepared by

the action of water upon calcium carbide, the manufacture of which is described in § 362.

Calcium carbide reacts with water according to the equation,

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

The apparatus illustrated in Fig. 104 may be used. The bottom of the flask is covered with a layer of sand, on which the calcium carbide rests.

The gas as evolved contains phosphine and hydrogen sulphide derived from impurities in the coke used to make the carbide. These may be removed by washing the gas with *acid* copper sulphate solution.

Acetylene is not, as a rule, stored in quantity, but is made as required for burning. Improvements in electric lighting have tended to diminish the use of acetylene for lighting. It is, however, much used for welding by the oxy-acetylene blow-pipe, and for this purpose is required in cylinders. Acetylene cannot be stored under pressure, for its instability is such that it will explode as a result of shock, forming carbon and hydrogen. It can, however, be stored in solution in acetone, which will absorb over a hundred times its volume under pressure, and this 'dissolved acetylene' is sold in cylinders and is a convenient source of the gas.

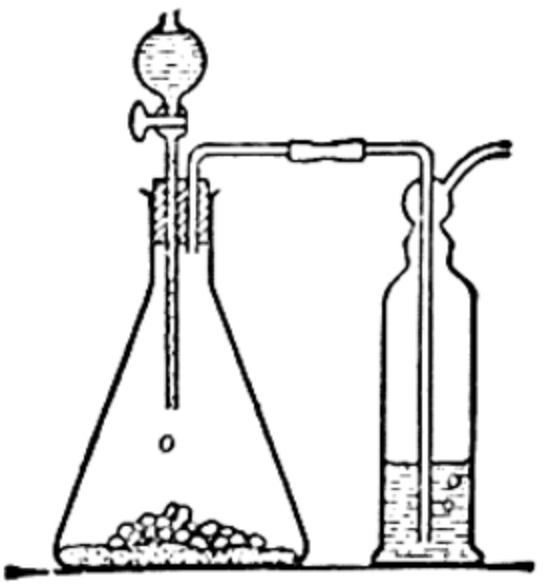


FIG. 104.—Preparation of acetylene.

*Formula.*—The formula may be proved to be $C_2H_2$ by the methods of § 539, and by analogy with ethylene the formula is written :

$$H—C \equiv C—H.$$

*Properties.*—Acetylene is a colourless gas which, when pure, has a pleasant smell, but as ordinarily made has a garlic-like odour. It liquefies at —81·5° C. at the ordinary pressure. Acetylene is only sparingly soluble in water, but is readily soluble in acetone.

Acetylene is an unstable compound, energy being evolved when it decomposes into carbon and hydrogen.

$$C_2H_2 = C_2 + H_2 + 56 \text{ Cals.}$$

It is sufficient to pass it through a heated tube to decompose it, and the compressed gas explodes as a result of shock or even a loud noise.

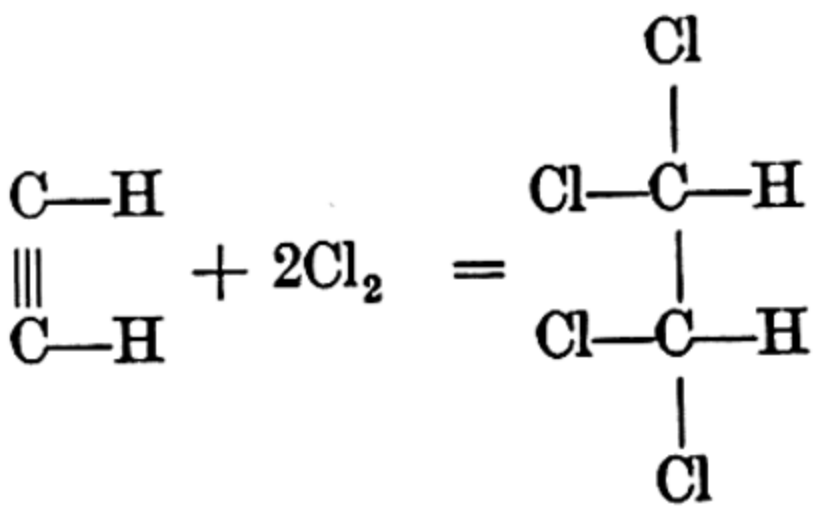
Acetylene ordinarily burns with an exceedingly smoky flame, but if a sufficient supply of air is provided the flame is exceedingly

brilliant and is without smoke. The jets at which the gas is to be burned are constructed so as to produce a flat sheet of flame exposing a large surface to the air.

Acetylene forms additive compounds with chlorine, oxidising agents, sulphuric acid, etc., in much the same way as does ethylene.

With chlorine, the gas inflames spontaneously, giving carbon and hydrogen chloride : if the gases are diluted, acetylene tetrachloride (tetrachlorethane) is produced,

$$C_2H_2 + 2Cl_2 = C_2H_2Cl_4.$$



With hydrogen bromide it gives ethylene dibromide

$$C_2H_2 + 2HBr = C_2H_4Br_2.$$

Acetic acid is now made commercially from acetylene. Acetylene can be made to react with water in presence of mercuric sulphate as a catalyst. Acetaldehyde is formed, which can be oxidised to acetic acid,

$$C_2H_2 + H_2O = C_2H_4O\,;\ 2C_2H_4O + O_2 = 2C_2H_4O_2.$$

Acetylene forms, with the metals, a series of remarkable compounds, of which the highly explosive cuprous acetylide is the best known. If acetylene be passed through an ammoniacal solution of cuprous chloride a red precipitate of cuprous acetylide, $Cu_2C_2.H_2O$, is produced. This when dry is highly explosive.

The action of hydrochloric acid upon this compound produces pure acetylene, and this affords one of the best ways of obtaining small quantities of the pure gas. Mercury forms a similar acetylide.

## COAL-GAS

**545. The Gas Industry.**—Coal-gas, which consists essentially of a mixture of hydrogen, methane, other hydrocarbons and carbon monoxide, is the gaseous product of the dry distillation of coal. The gas is mentioned by several eighteenth-century authors, and came into use for lighting in the first decade of the nineteenth century.

The gas industry is to-day of the highest importance. It provides the civilised world, not only with two of its chief sources of heating and power, coal-gas and coke, but also with ammonium sulphate, representing a large part of its fertilisers, and a long list of other products, including motor spirit, the raw materials of almost all our drugs and dyes, pitch for road-making, ammonia and sulphur.

Modern gas-making practice tends to specialise in the careful and complete separation of these by-products, and great modern gas-works, such for example as those which supply London, present a remarkable variety of chemical undertakings.

The fuel gases which are employed in industry include coal-gas, water-gas, producer-gas, blast-furnace gas, and, where available, natural gas. These are all essentially mixtures of hydrogen, methane

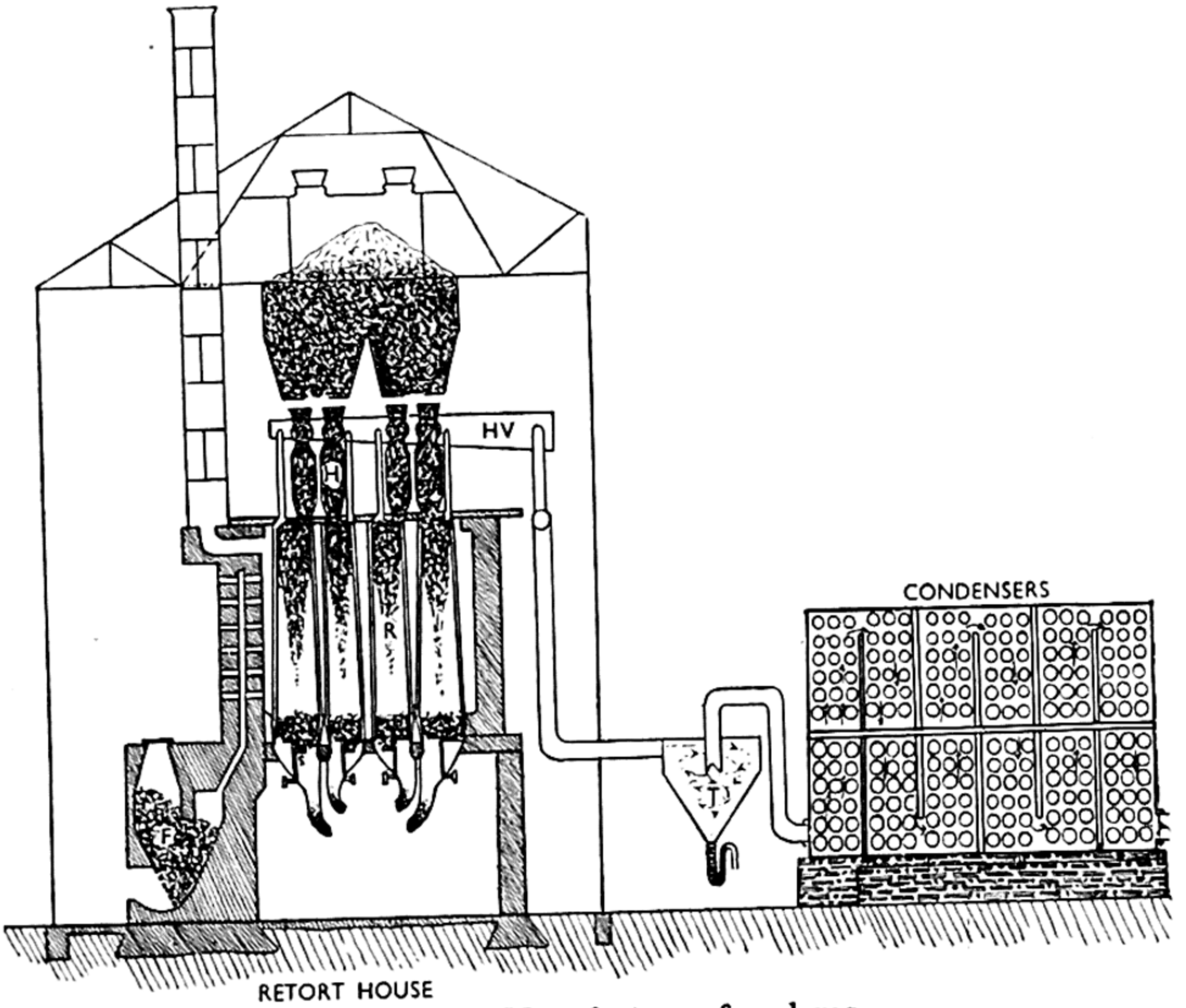



FIG. 105.—Manufacture of coal-gas.

and carbon monoxide in various proportions. The analyses given below show their approximate compositions :—

FUEL GASES.

| | $H_2$ | $CH_4$ | Other Hydro-carbons. | CO | $CO_2$ | $N_2$ |
|---|---|---|---|---|---|---|
| Coal-gas [1] . . . | 45–50 | 30–35 | 4 | 5–10 | — | 8 |
| Blue water-gas . . | 45 | 0·5 | — | 44 | 4 | 7 |
| Producer-gas . . . | 5 | 2 | — | 29 | 2 | 62 |
| Blast-furnace gas . . | 4 | 1 | — | 30 | 10 | 55 |
| Natural gas . . . | 3–30 | 65–95 | traces. | — | — | traces. |

[1] With no admixture of water-gas.

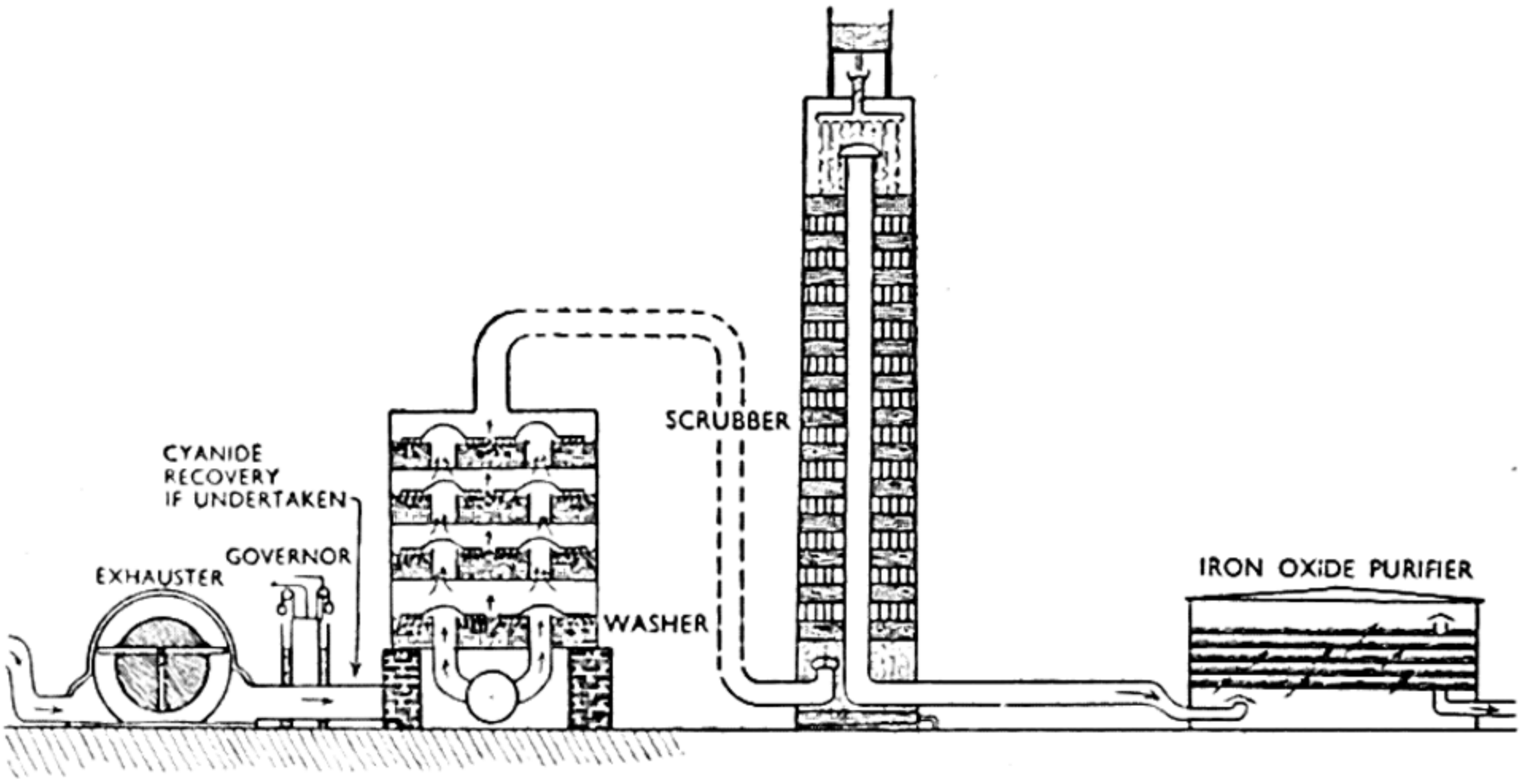
**546. Coal-gas Manufacture.**—Coal, as we have already seen (§ 533), is an exceedingly complex mixture, and when it is heated in absence of air an enormous variety of products are formed. The nature and quantity of these products vary with the coal used, but they invariably consist of :—

(1) A mixture of gases which do not condense on cooling, consisting substantially of hydrogen, methane, ethylene and carbon monoxide.

(2) A condensable liquid portion which separates into :—

(*a*) a watery layer containing ammonia as free ammonia, ammonium sulphide, cyanide, thiocyanate and carbonate, also pyridine and certain other organic bases.

(*b*) A tarry layer insoluble in water and containing a vast




Continuation of Fig. 105 (above: Gasometer.)

number of hydrocarbons, notably benzene $C_6H_6$, toluene $C_7H_8$, naphthalene $C_{10}H_8$, anthracene $C_{14}H_{10}$, and other compounds such as phenol (or carbolic acid) $C_6H_5 . OH$, cresols $C_7H_7 . OH$, etc.

(3) A non-volatile residue of coke consisting substantially of carbon and ash.

If the coal is distilled at high temperatures above 700° C., as is usual, the proportion of gaseous products is greater and the proportion of liquids less than if distillation is conducted at 300°–400° C. (low-temperature carbonisation). The latter method is being developed because it gives a better yield of the valuable benzene. The product left, too, differs from ordinary coke in being more readily inflammable, though like coke it is smokeless.

**547. The Retorts.**—In the most modern gas-works distillation is conducted in large vertical retorts (R). These have the advantage over the older horizontal retorts that they admit of continuous working. The type of retort illustrated in Fig. 105 consists of a tapered conical fireclay shaft, at the top of which is a gas-tight coal hopper (H), into which coal is fed at intervals. The retorts are built into a firebrick setting in which producer-gas (§ 555), generated by a coke-furnace (F) and mixed with air admitted at inlets (I), burns, heating them to a high temperature (*c.* 1000° C.). The coal slowly passes down the retort and decomposes, giving off its various decomposition products, which pass as a thick brownish smoke to the hydraulic main (HY). The coke is passed by a revolving Archimedean screw (S), to a hopper from which it is periodically withdrawn. In many works steam is blown into the base of the retort, decreasing the yield of coke and increasing that of gas by the reaction,

$$C + H_2O = CO + H_2.$$

**548. Condensation.**—The least volatile of the products of the coal condense in the wide pipe known as the hydraulic main, where the temperature falls to about 60° C. Tar and a fluid known as ammoniacal liquor (§§ 546 (2) (*a*), 690) condense here and are run off for separate treatment. The gas passes on for further treatment to the condensers proper, passing on the way through a tar extractor (T), which causes the droplets of tar, which form a fog, to settle out and leave the gas fairly clear.

The condensers are of many types, but commonly consist of an iron box through which pass many air tubes, thus exposing the gas within to a large cold surface. At this stage nearly all the benzene and naphthalene condense together with more ammoniacal liquor and some more tar. The cooled gas still contains some 0·6 per cent. ammonia and about half as much hydrocyanic acid, 1 to 2 per

cent. of hydrogen sulphide and 1 to 3 per cent. of carbon dioxide, all of which are to be removed in the subsequent purification.

**549. Extraction of Ammonia.**—The gas now passes to a pump known as an exhauster. This keeps the pressure in the retorts low thus preventing leakage, and impels the gas through the purification apparatus, which presents a considerable resistance.

The gas is then further purified from tar fog and freed from the greater part of its ammonia in a washer.

In the washer the gas bubbles repeatedly through water, in which the very soluble ammonia dissolves together with some hydrogen cyanide and sulphide. The water runs *downward* through the apparatus, so that the gas as it leaves the apparatus meets nearly fresh water which removes the ammonia very efficiently.[1] The last traces of ammonia are then removed by a scrubber. This consists of a tower packed with boards set edge-wise. Down this flows water while the gas passes up it. The liquors containing ammonia are collected and worked up for ammonium sulphate.

**550. Extraction of Cyanides.**—The next stage is, as a rule, the removal and recovery of cyanides. The removal of cyanides may be done by numerous processes. A common process is to pass the gas through a washer containing ferrous sulphate solution and an alkali, the hydrocyanic acid being converted into ferrocyanides. The alkali may be dispensed with if the extraction is performed before the ammonia is removed, a double ferrocyanide of iron and ammonium being produced and converted ultimately into sodium cyanide.

$$2FeSO_4 + 2H_2S + 4NH_3 = 2FeS + 2(NH_4)_2SO_4$$
$$2FeS + 2NH_3 + 6HCN = 2H_2S + (NH_4)_2Fe[Fe(CN)_6],$$

*v.* also § 241).

**551. Removal of Hydrogen Sulphide.**—Hydrogen sulphide is ordinarily removed by passing the gas through moist hydrated ferric oxide (bog iron ore). This is laid in layers upon shelves in rectangular iron vessels. The gas passes upward through several layers of the material, and the hydrogen sulphide reacts with the iron oxide, forming ferric sulphide and water,

$$Fe_2O_3 \,.\, nH_2O + 3H_2S = Fe_2S_3 + (n + 3)H_2O.$$

The ferric sulphide is allowed to accumulate until the absorption becomes inefficient. It is then spread out in the open air and kept moist and is thus oxidised to ferric oxide and sulphur,

$$2Fe_2S_3 + 3O_2 + 2nH_2O = 2Fe_2O_3 \,.\, nH_2O + 6S.$$

The mixture is then returned to the purifiers and alternately used and restored till it contains some 60 per cent. of sulphur, when it

[1] At this stage the gases may be scrubbed with oil to remove traces of naphthalene, but this is not always done.

is sold to the sulphuric acid manufacturers to be burnt to sulphur dioxide.

Carbon dioxide, hydrogen sulphide and carbon disulphide are occasionally all removed by the action of lime on the gas. The first two form the carbonate and sulphide respectively. The carbon disulphide probably forms calcium perthiocarbonate $CaCS_4$. The process is but little used owing to the very objectionable character of the residue.

Carbon disulphide is now removed by passing the gas over a heated nickel catalyst. It is thus reduced by hydrogen to methane and hydrogen sulphide, which is then removed by means of ferric oxide.

The gas now passes to the gas-holders whence it is passed into supply through meters to the town.

Coal-gas is commonly mixed with a proportion of water-gas (§ 556) in order to lower its cost without diminishing its calorific power.

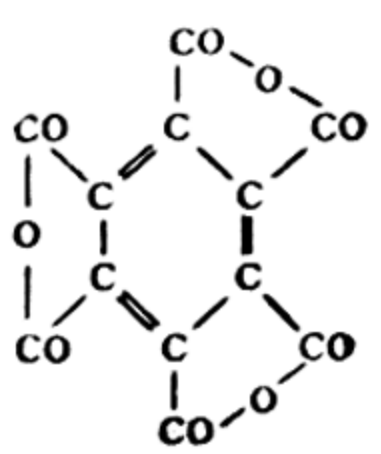
## OXIDES OF CARBON

Carbon forms four or possibly five oxides, namely :—

| | |
|---|---|
| Mellitic anhydride . . . . . | $C_{12}O_9$ |
| Carbon suboxide . . . . . | $C_3O_2$ |
| Carbon monoxide . . . . . | $CO$ |
| Carbon dioxide . . . . . | $CO_2$ |

An oxide of the formula $C_5O_2$ has been described, and also several rather indefinite solid oxides.

**552. Mellitic Anhydride $C_{12}O_9$** is usually studied in Organic Chemistry. Its structure is



**553. Carbon Suboxide** is obtained by the action of phosphorus pentoxide on malonic acid,

$$CH_2\begin{<}{CO\cdot OH}{CO\cdot OH} + 2P_2O_5 = C\begin{<}{CO}{CO} + 4HPO_3.$$

Carbon suboxide is a colourless gas, having a suffocating odour, which condenses to a liquid boiling at 6° C. It decomposes when gently warmed. Carbon suboxide burns with a smoky blue flame, forming carbon dioxide. It is not a substance of any practical importance.

**554. Carbon Monoxide CO. Occurrence and Preparation.**—Carbon monoxide is not found in nature. It is an important constituent of ordinary coal-gas, producer-gas and water-gas, and is found in the products of combustion of coal or coke where, as is usually the case, the supply of air is not sufficient for complete combustion.

Carbon monoxide is prepared—

(1) By the action of carbon dioxide on heated carbon.
(2) By the removal of the elements of water from formic or oxalic acid.
(3) By the action of sulphuric acid upon ferrocyanides.
(4) By the action of steam on white-hot carbon.

(1) A tube of combustion glass is packed with charcoal and heated to redness. A stream of carbon dioxide is passed through it and the issuing gases are washed with strong caustic soda or potash solution,

$$CO_2 + C = 2CO.$$

It is difficult to keep the charcoal sufficiently hot in the ordinary type of tube furnace.

(2) A better method is the following : Thirty grams of oxalic acid are covered with concentrated sulphuric acid in a 500 c.c. flask, fitted with a safety tube, and connected to two wash-bottles containing concentrated caustic potash. On heating the mixture carbon monoxide and dioxide are evolved, the latter being absorbed by the potash,

$$H_2C_2O_4(+ H_2SO_4) = CO + CO_2 + (H_2O + H_2SO_4).$$

The gas is very conveniently made by the action of sulphuric acid on sodium formate. Twenty-five grams of sodium formate are placed in a 500 c.c. flask, fitted with a thistle funnel and delivery tube leading to a pneumatic trough. On adding sulphuric acid, carbon monoxide comes off freely ; gentle heating may be needed in the later stages of the experiment,

$$NaHCO_2 + H_2SO_4 = NaHSO_4 + H_2CO_2$$
$$H_2CO_2 + H_2SO_4 = (H_2O + H_2SO_4) + CO.$$

This may be collected over water or, if required dry, dried with any of the usual drying agents.

(3) The action of concentrated sulphuric acid on potassium ferrocyanide also affords a convenient way of preparing the gas. The apparatus shown in Fig. 103 may be employed. Dilute acid must not be used, for under these conditions the very dangerous hydrocyanic (prussic) acid HCN is evolved.

The equation,

$$K_4Fe(CN)_6 + 8H_2SO_4 + 6H_2O = 3(NH_4)_2SO_4 + 4KHSO_4 + FeSO_4 + 6CO,$$

is commonly given, but the reaction is certainly more complex than it indicates.

(4) The action of steam on heated carbon yields the gas. The process is discussed under Water-gas, § 556.

**555. Commercial Preparation. Producer-gas.**—Producer-gas is essentially a mixture of carbon monoxide and nitrogen, made by blowing air through a layer of red-hot coke.

In many technical processes there is a preference for a gaseous rather than a solid fuel. The large gas engine has a much greater thermal efficiency than the steam engine burning solid fuel. Many processes also require the heating of a space which cannot readily be reached by solid fuel (*e.g.*, gas retorts), while others require freedom of the heated substance from ash. There is, therefore, a demand for a means of turning solid fuel into gas without much loss of energy. Coal can be distilled, yielding coal-gas; this gas is comparatively expensive and of high calorific power. Producer-gas obtained from coke is extremely cheap, but is of so low a heating power per unit volume that it does not pay to distribute it, and it is accordingly made on the spot where it is required. Moreover, when coke is converted into producer-gas, about 29 Cals. per gram-molecule of carbon are evolved: and when the gas from this quantity of carbon is burned to carbon dioxide, a further 68 Cals. are evolved. It is therefore very desirable to burn producer-gas while it is still hot, when little or no energy is lost: if the gas has to be cooled down rather more than 30% of the energy of the coke is wasted.

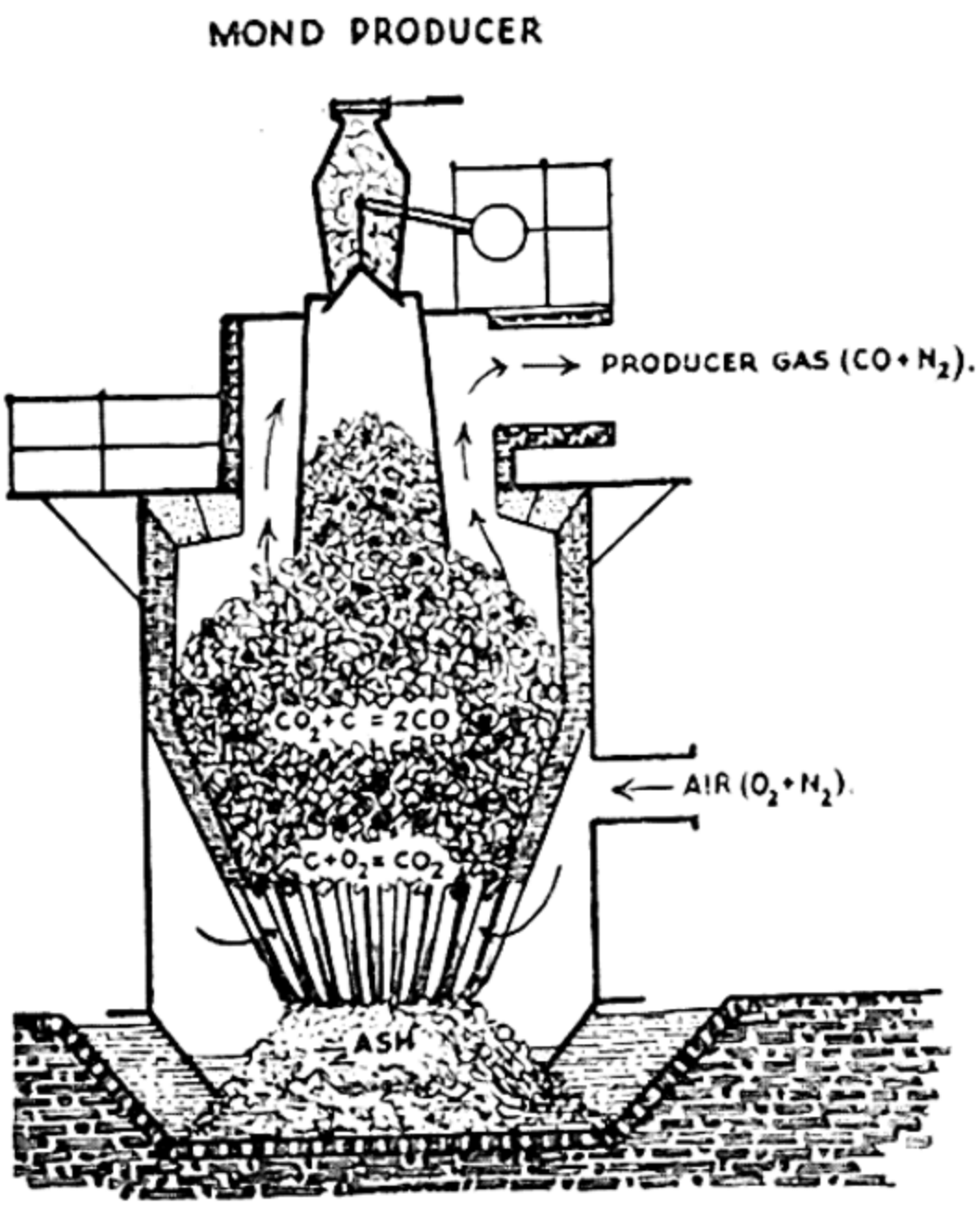



FIG. 106.—Mond producer.

The *producer* is, in principle, simply a large air-tight stove (Fig. 106). An air inlet is provided at the base and an exit for the gases at the top. Arrangements for admitting fuel and for removing

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ash without admitting air are also provided. Air enters at the base and burns to carbon dioxide ; the latter gas passes up through the red-hot fuel and reacts with it, forming carbon monoxide. The mixture of this carbon monoxide and the nitrogen derived from the air used is called producer-gas.

*Formation of Producer-gas.*

$$C + O_2 = CO_2 + 97 \text{ Cals.}$$
$$\underline{CO_2 + C = 2CO - 39 \text{ Cals}.}$$
$$2C + O_2 = 2CO + 58 \text{ Cals.}$$

*Combustion of Producer-gas.*

$$2CO + O_2 = 2CO_2 + 136 \text{ Cals.}$$

If the gas is to be burned in a gas engine the dust and ash, which would damage the cylinders, must be removed, and the gas is therefore scrubbed with a water spray to remove these gritty particles.

The energy of the combustion of the fuel to producer-gas is thus lost but gas-engines are so much more efficient than steam-engines, that the gain in conversion of heat into work more than compensates for the above loss.

A first-rate reciprocating steam engine will convert 12 per cent. of the heat evolved by the fuel into work, a good steam turbine, 18 per cent., while a suction producer and gas engine will utilise 24 per cent. of the heat energy of the fuel. It is not surprising then that the gas engine and producer are for many purposes replacing the steam engine.

When producer-gas is used for heating a furnace, the latter consists of two parts, the producer and the combustion chamber. In the former, air is admitted only in sufficient quantity to allow carbon monoxide to be formed ; in the latter, *secondary air* is admitted and the gas burns to carbon dioxide. An example of this process is given in the diagram illustrating the retort house in a gas-works (Fig. 105).

**556. Water-gas.**—If steam be passed over white-hot coke the reaction,

$$C + H_2O = CO + H_2 - 29 \text{ Cals.},$$

takes place. This reaction absorbs heat and, accordingly, the temperature of the fuel rapidly falls and the reaction soon ceases. The gas so produced has great calorific power, for it differs from producer gas in that it is not diluted by some 80 per cent. of nitrogen derived from the air. Moreover, it contains a large proportion of hydrogen, the heat of combustion of which is very high. Various methods of producing water-gas have been devised and the commonest of these is based on the principle of alternately raising the fuel to white heat by a blast of air, at the same time allowing the gases evolved to escape ; then passing a jet of steam through the white-hot fuel until it has cooled to a red heat. The water-gas produced

during this stage of the process is collected. One type of water-gas plant, the 'Dellwik,' is illustrated in Fig. 107. Air passes up through the red-hot fuel and out through the chimney shaft, raising the fuel to a high temperature. The air is then cut off; the exit to the shaft is closed and steam is admitted below the firebars, the gases being carried off through a steam superheater, thus returning some of their waste heat to the fuel. The gas is washed from ash, ammonia, etc., in a scrubber and is then ready for use.

Water-gas is often used to mix with coal-gas. Gas-works produce as a rule more coke than they can profitably sell and they usually covert some of it into water-gas. Water-gas has no illuminating power but good heating power. The high percentage of carbon monoxide contained in it renders the gas with which it is mixed very poisonous. Water-gas is not as a rule supplied unmixed with coal-gas on account of its poisonous properties, and its lack of a smell strong enough to give warning of a dangerous escape. Attempts

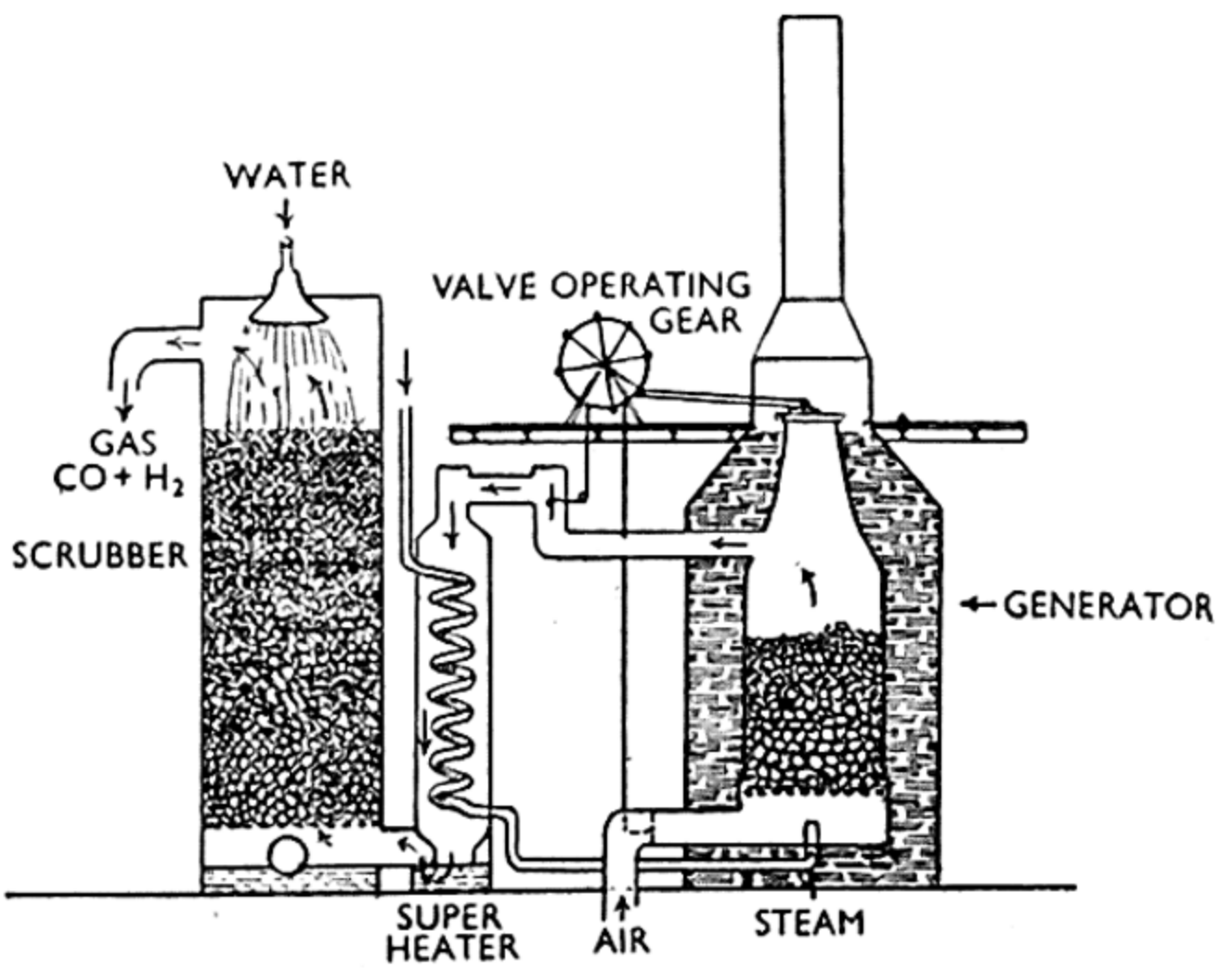


FIG. 107.—Dellwik blue water-gas plant.

have been made to add the smell artificially by passing the gas over some volatile and intensely odorous substance, such as phenyl carbamine, but the results do not appear to have been satisfactory. Water-gas is used as a source of hydrogen and of carbon monoxide, these gases being separated by various processes described in § 182 (3). It is also used as a source of both hydrogen and carbon dioxide for the combined Haber and Solvay processes (§§ 182 (3, *a*), 689, 236).

*Blast-furnace gas* is similar in composition to producer-gas and is used for similar purposes (*v.* §§ 545, 1137).

**557. Formula of Carbon Monoxide.**—Carbon dioxide may be shown to result from the combination of one atom of carbon with one molecule of oxygen (§ 563). By explosion in the eudiometer it may be shown that one volume of carbon monoxide combines with half a volume of oxygen to form one volume of carbon dioxide. So one molecule of carbon monoxide and one half molecule of oxygen form one molecule of carbon dioxide. The formula of the latter is $CO_2$ and so the formula of carbon monoxide is $CO_2$ less O, *i.e.*, CO.

The formula has been written $= C = O$, $C = O$ and $C \equiv O$. Examining these from the point of view of the electronic theory of valency, the first two formulæ are identical and represent a molecule which would be highly polar (having four electrons at one end and two at the other),

(1) : C⁘ O⁘ ,

while the third would also represent a polar molecule,

(2) C⋮ O: .

Carbon monoxide is actually non-polar, and none of these formulæ are satisfactory. The electronic theory of valency allows of a fourth formula, $C \rightleftarrows O$ or

(3) : C⋮ O:

which would be non-polar. This formula is also supported by the fact that carbon monoxide is a *donor* and combines with substances by contributing a pair of electrons to them, *e.g.*, in the carbonyls and such compounds as

$$[Pt(NH_3)_2(CO)_2]Cl_2,$$

but cannot act as an acceptor, *i.e.*, combine with substances by receiving a pair of electrons to complete its set of eight. Thus it forms no compound with water or ammonia. If it had formula (1) it should have acceptor properties. The parachor value for carbon monoxide also supports the last formula The formula $C \rightleftarrows O$ is then the most probable.

**558. Physical and Physiological Properties.**—Carbon monoxide is a colourless gas without taste or smell. It is highly poisonous, combining with hæmoglobin, the oxygen-carrying pigment of the blood, to form a cherry-red compound, carboxyhæmoglobin. This latter is useless for respiratory purposes and death ensues when about half the hæmoglobin of the blood has combined with carbon monoxide. The onset of the poison is insidious, nothing much being noticed until sudden weakness makes it difficult for the victim to escape. To this gas, poisoning by coke or charcoal fumes, motor exhausts and coal-gas, are all due. The remedy is immediate removal of the victim and the application of stimulants and artificial respiration. The bright pink colour of the flesh of persons poisoned in this way is characteristic and is due to carboxyhæmoglobin.

Carbon monoxide is of almost the same density as air, being fourteen times as heavy as hydrogen. It is liquefied with difficulty,

but more readily than hydrogen (B.P. — 190° C., F.P. — 207° C.). It is only slightly soluble in water.

*Chemical Properties.*—Carbon monoxide is stable and is not decomposed by rise of temperature. It burns readily to carbon dioxide, and mixtures of air and carbon monoxide containing as little as 12·5 per cent. of the latter are explosive.

$$2CO + O_2 = 2CO_2.$$

The explosion does not take place very readily unless water vapour is present, a fact which was the earliest example known of the effect of drying on the rate of reaction of gases. Carbon monoxide is a neutral oxide and does not react with either acids or bases to form salts.

Carbon monoxide is *unsaturated* and, like ethylene, readily forms addition products. Thus mixtures of chlorine and carbon monoxide combine under the influence of light, forming phosgene or carbonyl chloride.

$$CO + Cl_2 = COCl_2.$$

A mixture of sulphur vapour and carbon monoxide passed through a heated tube reacts and carbonyl sulphide COS is formed. Carbon monoxide reacts with heated caustic soda, producing sodium formate; the yield is poor unless the process is conducted under pressure,

$$NaOH + CO = H.COONa.$$

Carbon monoxide forms an addition product with cuprous chloride, solutions of which in hydrochloric acid or in ammonia absorb the gas.

Carbon monoxide reacts with some of the metals, forming remarkable compounds known as carbonyls, the most important of which *nickel carbonyl* $Ni(CO)_4$, is the foundation of the Mond nickel process (§ 1201). It reacts with steam at high pressures and temperatures in presence of metallic catalysts giving carbon dioxide and hydrogen (§ 182 (3*a*) ). This is an industrial method for making hydrogen

$$CO + H_2O = CO_2 + H_2.$$

It undergoes numerous reactions with hydrogen in presence of catalysts. By varying the temperature, pressure and catalyst it is possible to form (*a*) methane, (*b*) mixtures of hydrocarbons from which synthetic petrol can be distilled, (*c*) methyl alcohol. All these reactions are the foundation of important industrial processes.

Carbon monoxide and ammonia react at moderate temperatures and pressures giving hydrocyanic acid (§ 574). For their structure, see (§ 1217a).

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**559. Detection and Estimation.**—Carbon monoxide is recognised by its character as an odourless gas, burning with a blue flame and producing carbon dioxide (lime-water test), and capable of being absorbed by ammoniacal cuprous chloride. Small proportions of the gas are best detected by its effect on blood. The spectrum of hæmoglobin (normal blood) shows two dark absorption bands; on addition of a little ammonium sulphide these disappear and *one* band appears in the space between them. Blood treated with carbon monoxide contains carboxyhæmoglobin, and this gives much the same spectrum as hæmoglobin, but the addition of ammonium sulphide to carboxyhæmoglobin does not cause the two bands to be replaced by one. To detect carbon monoxide in the air 2 or 3 c.c. of much diluted blood is shaken with the air in a bottle. It is then removed and a few drops of ammonium sulphide added. If the spectroscope shows two absorption bands carbon monoxide was contained in the air examined.

The proportion of the gas in a mixture is ascertained by first removing all acid gases with potash, and then absorbing the carbon monoxide with ammoniacal cuprous chloride, noting the diminution in volume so produced.

**560. Carbonyl Chloride, Phosgene, $COCl_2$.**—Carbonyl chloride results when carbon monoxide and chlorine combine, but it is best prepared by

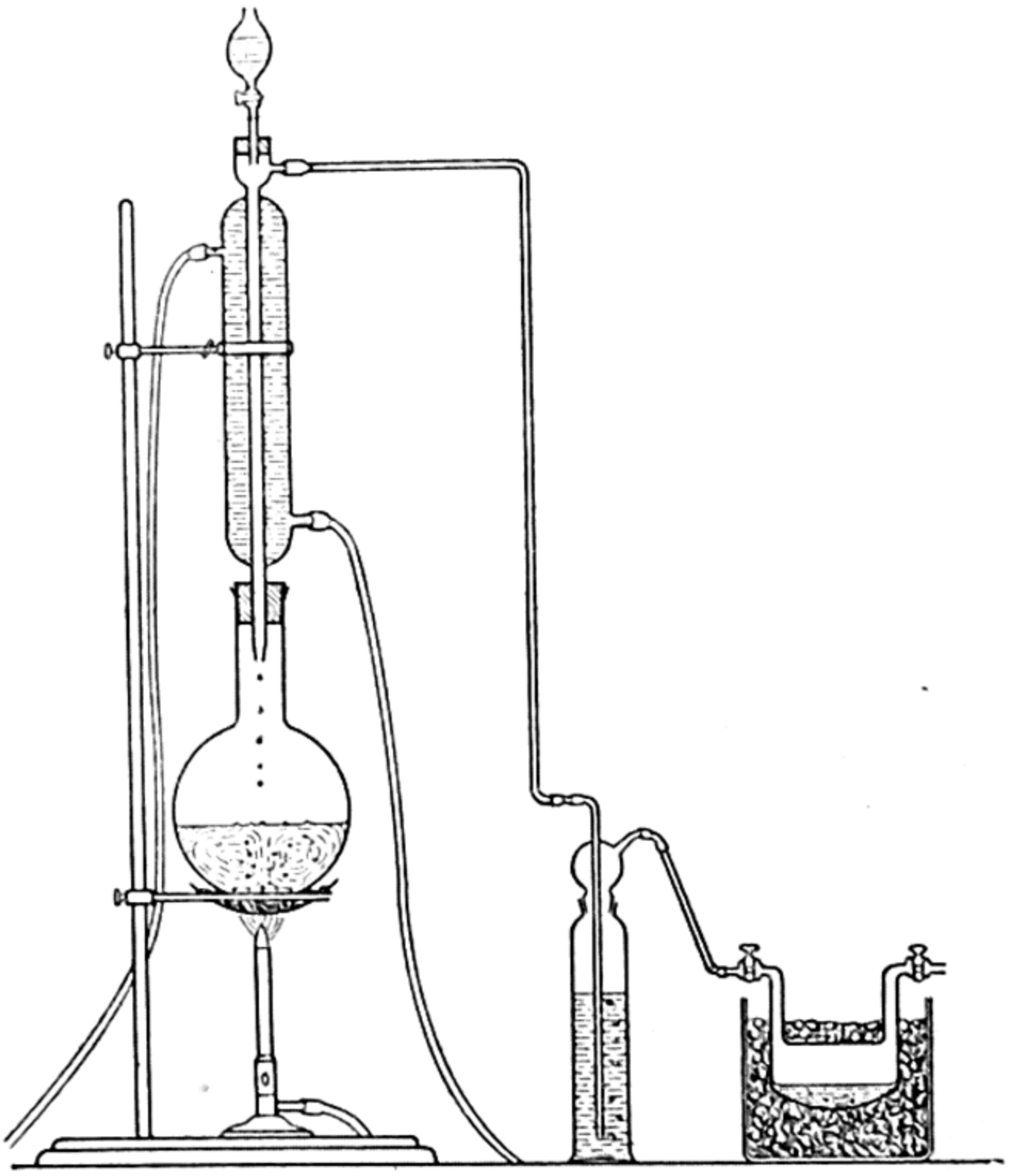

FIG. 108.—Preparation of carbonyl chloride.

boiling 100 gms. of carbon tetrachloride $CCl_4$ with 120 c.c. of 80 per cent. fuming sulphuric acid. The carbon tetrachloride is boiled under reflux and the acid is run in drop by drop through a tap funnel. The gas evolved passes out of the condenser and is washed with concentrated sulphuric acid and condensed in a good freezing mixture. The preparation is not suitable for the student.

$$CCl_4 + 2SO_3 = COCl_2 + S_2Cl_2O_5$$

It is a highly poisonous gas with an odour of musty hay. It readily condenses to a liquid, boiling at 8° C. It is used in the manufacture of certain organic chemicals and in the war of 1914–18 was employed as a poison-gas.

Carbonyl chloride is the acid chloride (cf. p. 195, note 1) of carbonic acid. It reacts with water, forming carbon dioxide and hydrochloric acid,

$$COCl_2 + H_2O = 2HCl + CO_2,$$

and with ammonia forming *carbamide* or urea,

$$COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl.$$

**561. Carbon Dioxide. History and Occurrence.**—Carbon dioxide in the form of the 'foul air' which accumulated in old wells, etc., had been noticed even before the sixteenth century. Van Helmont, at the close of the sixteenth century, recognised the existence of what he first termed a *gas* produced by the combustion of carbon and the action of vinegar upon chalk, by fermentation, etc. The gas was thoroughly studied by Bergman in 1774, and Lavoisier established its composition and named it *acide carbonique*.

The gas, carbon dioxide, occurs free in the atmosphere to the extent of about 3 parts in 10,000, and its presence is of the utmost significance to plant and animal life. The structure of both plants and animals consists essentially of carbon compounds, and all the carbon contained therein is derived, directly or otherwise, from the atmosphere. The carbon compounds contained in animals are derived from those of plants which the animals have eaten. The

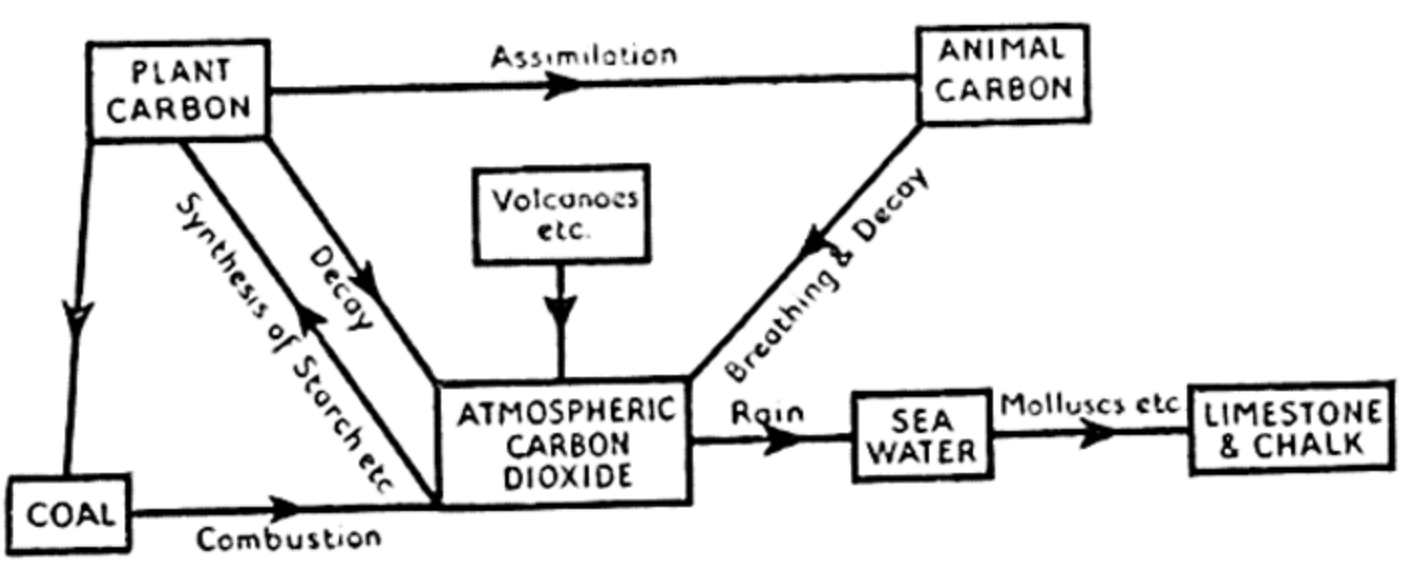


FIG. 109.—Carbon circulation of the world.

carbon compounds of plants are derived from the carbon dioxide of the air.

The leaves of plants contain the green pigment, chlorophyll, and this substance in the leaf, but not in the laboratory, has the power

of bringing about a reaction between carbon dioxide and water resulting in the formation of starch and oxygen,

$$6nCO_2 + 5nH_2O = (C_6H_{10}O_5)n + 6nO_2.$$

The starch is converted by the plant into the various materials, cellulose, etc., of which it is composed.

Animals feed on carbon compounds in the form of plant tissues or the flesh of animals which have themselves fed on plant tissues. This carbon is ultimately excreted by the lungs of the animals in the form of carbon dioxide. The bacterial decomposition of the dead bodies of animals and plants also yields carbon dioxide. Thus plant and animal life together maintain the proportion of carbon dioxide in the air at a steady value of about 0·03 per cent. by volume. Carbon dioxide has been lost permanently from the air as a result of the formation, by various aquatic creatures, of shells consisting of calcium carbonate. The vast beds of limestone and chalk are derived from this source, and the loss of carbon dioxide in this way is probably still active. On the other hand, man is now converting vast stores of the carbon in coal and oil into carbon dioxide by burning them, and he produces yearly some 500 cubic miles of carbon dioxide. Even this vast quantity appears to have hardly influenced the composition of the atmosphere, of which it forms, after all, less than the one hundred thousandth part. We may represent the carbon circulation of nature diagrammatically as in Fig. 109.

Carbon dioxide is not only evolved in these biological processes, for in volcanic districts the evolution of carbon dioxide is not uncommon. Thus in the Grotto del Cane, near Naples, a dog is suffocated in the heavy gas rising from the floor, while a man, rising above it, is unharmed. In the Valley of Death, in Java, the same phenomenon occurs on a larger scale, and the ground is littered with skeletons, including those of tigers, peacocks and human beings. The Death Gulch, in the Yellowstone Park (U.S.A.), also produces the gas, and the skeletons of grizzly bears testify to its deadly properties. Old wells, cellars, etc., are commonly filled with this gas, perhaps derived from the action of water containing vegetable acids on chalk or limestone.

**562. Preparation of Carbon Dioxide.**—Carbon dioxide is made :—

(1) By the combustion of carbon and its compounds.
(2) By the action of heat on carbonates.
(3) By the action of acids on carbonates.
(4) By biological processes—notably fermentation.

The first method is only used on the large scale, where a very dilute gas will suffice. The second is largely employed on the commercial scale. The third finds its use in the laboratory, while

the fourth has occasionally been employed on the commercial scale.

(1) Furnace gases contain chiefly carbon dioxide and nitrogen, and have occasionally been used as a source of the gas. The gases may be cooled and compressed and then brought into contact with water, which will dissolve a considerable volume of compressed carbon dioxide, but very little nitrogen. On reducing the pressure on the water the carbon dioxide is once more evolved.

Carbon dioxide is also obtained as a by-product of the manufacture of hydrogen from water-gas [§ 182 (3*a*) ].

(2) All carbonates, save those of the alkali metals, are decomposed by heat, and the action of heat on calcium carbonate (chalk or limestone) has been used to prepare the gas on a large scale. Limestone is heated in retorts and subjected to the action of superheated steam. The steam carries off the carbon dioxide and thus makes the equilibrium reaction,

$$CaCO_3 \rightleftharpoons CaO + CO_2,$$

complete itself at a manageable temperature.

(3) In the laboratory the action of a dilute acid upon calcium carbonate is used. The action of dilute hydrochloric acid upon marble in a Kipp's apparatus is the usual method,

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

The use of sulphuric acid is undesirable, since a layer of insoluble calcium sulphate forms on the marble and stops the reaction.

On the large scale sulphuric acid and powdered chalk have been used.

(4) The process of alcoholic fermentation consists in the decomposition of glucose or other sugars by the yeast plant, alcohol and carbon dioxide being formed according to the equation,

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$

The carbon dioxide evolved from brewers' vats, and in the fermentation of molasses, etc., to give industrial alcohol, have been used in the manufacture of soda-water.

**563. Formula.**—If carbon is burned in oxygen no change in volume results. It follows then that one volume of carbon dioxide contains one volume of oxygen, or, by Avogadro's law, that one molecule of carbon dioxide contains one molecule of oxygen $O_2$. The formula of carbon dioxide is then, $C_nO_2$. The density ($H_2 = 1$) is 22, and the molecular weight is therefore 44, and 1 gram-molecule contains $44 - 2 + 16$ gms. of carbon $= 12$ gms., 1 gram-atomic weight of carbon. The formula is therefore $CO_2$, which we may write, $O = C = O$. Physical evidence shows that the three atoms are arranged in a straight line.

**564. Physical Properties.**—Carbon dioxide is a colourless gas with a faint and pleasant taste and smell. It is not poisonous in small quantities, but is not, of course, a respirable gas. It stimulates the respiratory centres, causing deep and vigorous breathing, hence a mixture of carbon dioxide with much oxygen is useful for restoring breathing which has nearly ceased, as in drowning, severe shock, etc. The unpleasant feeling of a crowded, stuffy room is not due to the carbon dioxide present but to excessive humidity, lack of cooling air-currents, and to organic products exhaled by the crowd.

Carbon dioxide is readily liquefied by pressure or strong cooling to a liquid. If the liquid is allowed to escape from its containing cylinder through a bag of cloth, its rapid evaporation freezes it to a 'snow' of solid carbon dioxide. This substance, mixed with amyl acetate or ether, forms an excellent freezing mixture for low temperatures, — 100° C. being attainable. The solid evaporates without melting. Its sublimation temperature at 1 atm. is — 78·2° C. It is prepared on the large scale for refrigeration under the name of "dry ice" or Dricold.

Carbon dioxide dissolves in water and also reacts with it. One volume of water dissolves 1·002 vols. carbon dioxide at normal pressure and 15° C. A solution saturated at about 8 atm. is called soda-water. A little soda (*c.* 0·2 per cent.) is added to the water before the carbon dioxide is dissolved in it.

All natural waters contain dissolved carbon dioxide, and this makes possible the growth of aquatic plants. The effect of water containing the gas upon rocks consisting mainly of calcium carbonate is discussed in § 199.

**564a. Chemical Properties.**—Carbon dioxide is a stable substance and does not readily decompose. Thus it does not support the combustion of any substances except certain metals, potassium, sodium and magnesium, the heat of the combustion of which decomposes the gas, forming, as a rule, a carbonate and carbon,

$$4Na + 3CO_2 = 2Na_2CO_3 + C.$$

Potassium reacts with carbon dioxide at 230°–240° C., yielding up to 17 per cent. of potassium oxalate $2K + 2CO_2 = K_2C_2O_4$.

Carbon dioxide reacts with hydrogen according to the equilibrium reaction,

$$CO_2 + H_2 \rightleftharpoons CO + H_2O.$$

This reaction has been utilised to obtain pure carbon monoxide from water-gas (§ 182). Carbon dioxide reacts with water to form carbonic acid, which ionises to a very small extent,

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{--}.$$

Both carbon dioxide (being an acid anhydride) and also, of course, carbonic acid combine with alkalis. A normal carbonate is formed when the alkali is in excess ; but with excess of carbon dioxide the bicarbonate results, though only in quantity in the case of potassium, sodium and ammonium salts,

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$
$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3.$$

Accordingly, carbon dioxide is readily absorbed by caustic alkalis and lime. Solutions of the former are used to absorb it (cf. §§ 260, 358) ; thus, also the proportion of carbon dioxide present in a gas may be determined, the diminution of volume caused by contact with caustic potash being noted.

The reaction of carbon dioxide and water to form starch in the cells of green plants has been mentioned on p. 440.

$$6nCO_2 + 5nH_2O = (C_6H_{10}O_5)_n + 6nO_2.$$

The reaction has to some extent been imitated in the laboratory by passing carbon dioxide through a suspension of nickel carbonate or ferric oxide in water while it is illuminated by light. Certain sugars, which might well polymerise to starch, are formed by reactions which may be similar to those which occur in the green plant.

**565. Detection and Estimation.**—The action of the gas on lime-water, a solution of calcium hydroxide, is used as a means of detecting it. Calcium hydroxide reacts with carbon dioxide, forming calcium carbonate and water ; calcium carbonate being insoluble, is precipitated, and thus lime-water is rendered turbid by the action of the gas,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

If the turbid lime-water be exposed to the continued action of the gas, it becomes clear once more owing to the formation of soluble calcium bicarbonate,

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2.$$

Carbon dioxide is best estimated by its action on baryta water ($Ba(OH)_2$) A known volume of the gas containing the carbon dioxide may be shaken with or aspirated through a known volume of standard baryta (*c.* N/50) solution and the excess titrated with acid, using phenolphthalein as indicator.

**566. Uses of Carbon Dioxide.**—Carbon dioxide is used for the manufacture of soda-water and aerated drinks in general. It finds additional uses in fire extinguishers, some of which contain an acid and a bicarbonate separated by a glass partition. This, when broken, causes the evolution of the gas, the pressure of which projects a

stream of carbon dioxide froth into the fire, at once cooling it and excluding oxygen. The foam extinguisher (§ 492) depends on the formation of a permanent foam of carbon dioxide bubbles.

**567. The Carbonates.**—The carbonates of the metals are often found native. They are prepared, for the most part, by the action of sodium or ammonium carbonate solution on a soluble salt of the metal,

$$Ca^{++} + CO_3^{--} \rightleftharpoons CaCO_3\downarrow$$

*or*

$$CaCl_2 + Na_2CO_3 = CaCO_3\downarrow + 2NaCl.$$

Most of the metals form salts with carbonic acid. The metals whose oxides are very weak bases, such as aluminium and chromium, do not do so. The carbonates of the metals are, in general, insoluble in water—the exceptions being those of the alkali metals.

When heated, the carbonates of all the metals except potassium, sodium, rubidium and cæsium, decompose into carbon dioxide and the oxide of the metal. Barium carbonate decomposes only at a white heat, calcium carbonate at a strong red heat and the remainder very readily.

Acids, in general, decompose the carbonates, forming metallic salts, carbon dioxide and water.

The action of carbonic acid on carbonates generally yields bicarbonates, but these can rarely be isolated in the solid state.

Basic carbonates are formed by most metals. It is often doubtful whether they are compounds or merely mixtures of the hydroxide and carbonate of the metal, resulting from the reaction

$$XCO_3 + 2H_2O \rightleftharpoons X(OH)_2 + H_2CO_3.$$

If this reaction takes place comparatively slowly we obtain carbonates containing but little hydroxide, such as that of zinc,

$$Zn(OH)_2.3ZnCO_3.$$

If the hydrolysis is more rapid such carbonates as white lead, $Pb(OH)_2.PbCO_3$, result.

**568. Carbon Disulphide $CS_2$.**—Carbon disulphide is prepared by the action of sulphur on white-hot carbon. The laboratory preparation is difficult. On the large scale a furnace in the form of a shaft filled with coke is used. In the base of the shaft are fitted two large carbon electrodes, between which passes a current which raises the coke to a high temperature. Sulphur is fed in at the sides. It melts and vaporises and the vapour combines with the carbon,

$$C + 2S = CS_2.$$

The carbon disulphide vapour passes out of the top of the shaft and is condensed. It is redistilled in order to purify it.

Carbon disulphide is a colourless liquid which when pure is said to have a pleasant ethereal smell, but which, as ordinarily met with, has a repulsive and fetid odour. Its vapour is highly poisonous.

Carbon disulphide boils at 46° C. It does not dissolve in water but is itself an excellent solvent. Most organic substances and, among inorganic substances, sulphur, phosphorus, and iodine, readily dissolve in it.

Carbon disulphide vapour is highly inflammable, a temperature of 150° C., being sufficient to ignite it. Thus, when it is distilled it is not enough to extinguish all naked lights, but it is also necessary to remove any hot metal in the vicinity. It burns to sulphur dioxide and carbon dioxide,

$$CS_2 + 3O_2 = CO_2 + 2SO_2.$$

A mixture of carbon disulphide vapour and nitric oxide burns with an exceedingly brilliant blue flash.

Carbon disulphide reacts with chlorine, forming carbon tetrachloride and sulphur chloride—a reaction of commercial importance (*v. infra*). Carbon disulphide is an *acidic sulphide* (§§ 804, 821), and forms, with alkali sulphides, compounds which are known as thiocarbonates. Thus, on adding carbon disulphide to an alcoholic solution of sodium sulphide and diluting with ether, pinkish yellow needles of sodium trithiocarbonate are precipitated,

$$Na_2S + CS_2 = Na_2CS_3.$$

In this reaction we see an analogy to carbon dioxide.

Its industrial uses are several.

(1) It is an excellent solvent and is used for extraction of grease, oil, waxes etc. Its poisonous character has led to its partial replacement by chlorinated compounds (§ 571).

(2) A certain quantity is used for the destruction of pests. If a small quantity is introduced into a grain-bin all weevils and other animal pests are destroyed, and when the grain is removed the vapour diffuses away and leaves nothing behind.

(3) Large quantities are employed in the artificial silk industry. When cellulose (*e.g.*, wood-pulp) is treated with sodium hydroxide and carbon disulphide, a dark orange yellow jelly (viscose) is formed. This when expelled through fine jets into an acid bath gives viscose silk fibre.

**569. Carbonyl Sulphide COS** is made by the action of sulphuric acid on potassium thiocyanate,

$$KCNS + 2H_2SO_4 + H_2O = COS + KHSO_4 + NH_4.HSO_4.$$

The gas is washed with caustic potash and sulphuric acid.

It is a colourless and very poisonous gas. It burns in air to sulphur dioxide

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and carbon dioxide. Water decomposes it to carbon dioxide and hydrogen sulphide,

$$COS + H_2O = H_2S + CO_2.$$

**570. Fluorides of Carbon $CF_4$, $C_2F_6$, $C_3F_8$, etc.**—These gases are obtained by passing fluorine over carbon. They are extremely stable.

**571. Carbon Tetrachloride $CCl_4$** is made by the action of chlorine upon carbon disulphide in presence of aluminium chloride as a catalyst,

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2.$$

Where natural gas is abundant, it is made by direct chlorination of methane in presence of various catalysts and at about 400° C.

$$CH_4 + 4Cl_2 = CCl_4 + 4HCl.$$

It is a heavy colourless liquid with a chloroform-like odour. Its vapour is decidedly poisonous. It boils at 77° C. and the density of its vapour is 78($H_2 = 1$), nearly six times that of air.

It has therefore been used as a fire extinguisher (Pyrene), for the heavy non-inflammable vapour engendered by the contact of the liquid with the burning material rapidly extinguishes small fires.

Carbon tetrachloride is a very stable substance chemically and so forms a useful solvent. It reacts with sulphur trioxide, forming carbonyl chloride (§ 560). None of the commoner reagents attack it. In this respect it is in strong contrast to the chlorides of all other elements. Several simple compounds of carbon, hydrogen and chlorine, such as tetrachlorethane, are made commercially and find uses as non-inflammable solvents for use in paints, for cleaning clothes, etc.

**572. Cyanogen and Its Compounds.**—The group of compounds containing the — CN radical, are all ultimately derived from cyanides or ferrocyanides. The radical — CN shows some likeness in its general chemical behaviour to an atom of a halogen, such as — Cl, and the case of the cyanogen compounds was one of the earliest in which the behaviour of a radical or group of atoms was seen to be analogous to that of a single atom.

Cyanogen compounds are all derived from the cyanides.

The chief sources of these compounds are :—

(1) The reaction of carbon with sodium and ammonia (§ 241).

$$2Na + 2C + 2NH_3 = 2NaCN + 3H_2$$

(2) Reaction of sodium chloride and calcium cyanamide (§ 366)

$$CaC_2 + N_2 = CaNCN + C$$
$$CaNCN + C + 2NaCl = CaCl_2 + 2NaCN$$

(3) Coal-gas (§ 550).

**573. Cyanogen $C_2N_2$.**—This gas is made by the action of heat upon mercuric cyanide $Hg(CN)_2$,

$$Hg(CN)_2 = Hg + C_2N_2,$$

The gas may be collected over water, in which, however, it is somewhat soluble.

Cyanogen is a colourless gas. It is exceedingly poisonous, as are nearly all substances which contain the cyanide radical. Cyanogen burns with a characteristic peach-blossom coloured flame, forming carbon dioxide and nitrogen,

$$C_2N_2 + 2O_2 = 2CO_2 + N_2.$$

In some respects it resembles a halogen: thus it reacts with potassium, forming the cyanide

$$2K + C_2N_2 = 2KCN,$$

and with caustic potash forming the cyanide and cyanate

$$2KOH + (CN)_2 = KCN + KOCN + H_2O.$$

It dissolves in four volumes of water and its solutions slowly decompose, forming ammonium oxalate.

$$NC - CN + 4H_2O = NH_4.O.OC - CO.O.NH_4.$$

The hydrolysis of the $-CN$ group to the group $-C(=O)-O-NH_4$ is of general occurence and is much used as a means of synthesising organic acids.

**574. Hydrocyanic Acid HCN.**—Hydrocyanic or prussic acid is found in Nature combined with glucose, in the glucoside *amygdalin*, which is present in bitter almonds, laurel leaves, and some other plants. We may remember that the 'last alchemist,' Dr. Price, poisoned himself, in 1783, with a draught prepared from crushed laurel leaves.

(1) Hydrocyanic acid is made by distilling potassium cyanide or ferrocyanide with moderately diluted sulphuric acid,

$$KCN + H_2SO_4 = KHSO_4 + HCN.$$

Considerable precautions should be taken, owing to its poisonous character, the preparation being conducted out of doors or in a fume cupboard *with a good draught. Only skilled persons should undertake its preparation.*

(2) Hydrocyanic acid has been made industrially by various synthetic methods, such as the reaction of carbon monoxide and ammonia, at moderately high temperatures and pressures (*e.g.*,

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70° C. and 17 atm.). Formamide is first formed and decomposes to hydrocyanic acid and water.

$$NH_3 + CO = H.CO.NH_2$$
$$H.CO.NH_2 = HCN + H_2O.$$

Hydrocyanic acid is a colourless liquid with a peculiar sickly smell. It is highly poisonous, being remarkable not so much for the small quantity needed to cause death as for the violence and rapidity with which it acts. Death occurs commonly within two minutes, and if the victim survives for half an hour, he will almost certainly recover. The poison acts on the central nervous system. The violence of the action makes it most necessary to take all precautions in handling it. Any remedy must therefore be administered *instantly*, and freshly-prepared ferrous hydroxide made by mixing ferrous sulphate solution and ammonia is the best antidote.

The formulæ, $H - C \equiv N$, $H - N \equiv C$ and $H - N = C$, have all been given for hydrocyanic acid. Its organic compounds are of two types, which have apparently the formulæ $X - C \equiv N$ and $X - N \rightarrow C$. The acid is probably an equilibrium mixture,

$$H - C \equiv N \rightleftharpoons H - N \rightarrow C,$$

the latter form greatly preponderating.

In solution it slowly changes into ammonium formate, a fact which explains its occasional failure as a means of suicide,

$$H - C \equiv N + 2H_2O = H.CO.ONH_4.$$

Hydrocyanic acid is an exceedingly weak acid.

It finds considerable use as a fumigant for the destruction of rats in ships and warehouses, bugs in dwelling-houses, and insect pests in greenhouses.

**575. The Cyanides.**—Potassium and sodium cyanide find considerable use in industry and are to-day the chief source of cyanogen compounds. Their preparation is described under sodium compounds (§ 241). Other cyanides are made by double decomposition, etc.

The cyanides are the salts of a very weak acid and are accordingly strongly hydrolysed in solution,

$$KCN + H_2O \rightleftharpoons KOH + HCN.$$

*or*

$$\begin{cases} CN^- + H^+ \rightleftharpoons HCN \\ H_2O \rightleftharpoons H^+ + OH^-. \end{cases}$$

Their solutions are, accordingly, strongly alkaline and smell of hydrocyanic acid. They are, like hydrocyanic acid, intensely

poisonous. The same antidote may be used with more hope of success, since their action is slower.

When solutions of the salts of metals other than those of Groups Ia, IIa, and III, are mixed with excess of a cyanide, a complex negative cyanide ion is usually formed

$$M^{+n} + xCN^- \rightleftharpoons [M(CN)_x]^{(x-n)-}$$

These are in some cases very stable, as the ferrocyanide ion (*v. infra*), but often exist only in equilibrium with a noticeable proportion of the ions from which they were formed. Thus, when potassium cyanide is added to a solution of a silver salt, silver cyanide, an insoluble white salt, is at first precipitated, and then re-dissolves in excess of potassium cyanide solution, owing to formation of the argentocyanide ion, but silver ion and cyanide ion are always to be detected in its solution.

Gold cyanide behaves similarly, and the solvent power of potassium cyanide for gold (§ 324) is due to this property.

**576. The Ferrocyanides.**—Ferrocyanides are now usually produced from coal gas (§ 241). In the laboratory potassium ferrocyanide may be made by adding pure ferrous sulphate solution to potassium cyanide solution till a small permanent precipitate remains. The solution is filtered and evaporated and potassium ferrocyanide crystallises out,

$$Fe^{++} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{\equiv}$$

*or*

$$FeSO_4 + 6KCN = K_4Fe(CN)_6 + K_2SO_4.$$

Potassium ferrocyanide forms large yellow tabular crystals, of which 28 gms. dissolve at 15°, and 100 gms. dissolve at 100° C. in 100 gms. of water.

When solutions of ferrocyanides are acidified with hydrochloric acid white hydroferrocyanic acid $H_4Fe(CN)_6$ is precipitated. The ferrocyanides of copper and iron are of interest and are discussed in §§ 56, 290, 1171.

**577. The Ferricyanides.**—When potassium ferrocyanide is oxidised with chlorine, permanganates, or electrolytically, etc., potassium ferricyanide $K_3Fe(CN)_6$ is formed.

Thirteen grams of powdered potassium ferrocyanide are dissolved in 100 c.c. of cold water and 4 c.c. of concentrated hydrochloric acid are added. To this solution 1 gm. of potassium permanganate, dissolved in 150 c.c. of water, is added a little at a time until a drop of the solution gives no blue colour with ferric chloride. The solution is filtered and evaporated on the water-bath to about 15 c.c. Potassium ferricyanide crystallises on cooling.

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$$2[Fe(CN)_6]^{\equiv} + 2H^+ + O = 2[Fe(CN)_6]^{=} + H_2O$$

*or* $KMnO_4 + 8HCl + 5K_4Fe(CN)_6 = 6KCl + MnCl_2 + 5K_3Fe(CN)_6 + 4H_2O.$

Potassium ferricyanide forms mahogany-red crystals, of which there dissolve in 100 gms. of water, 40 gms. at 15° C. and 80 gms. at 100° C. It is a mild oxidising agent. Its reaction with iron salts is of interest and is mentioned in § 1171.

**578. Nitroprussides.**—Sodium nitroprusside $Na_2[Fe(CN)_5NO]2H_2O$ is obtained when potassium ferricyanide is boiled with diluted nitric acid (1 : 1) and the solution is made alkaline with sodium hydroxide. It is a red crystalline salt which gives a deep purple coloration with soluble sulphides, for which it may be used as a test.

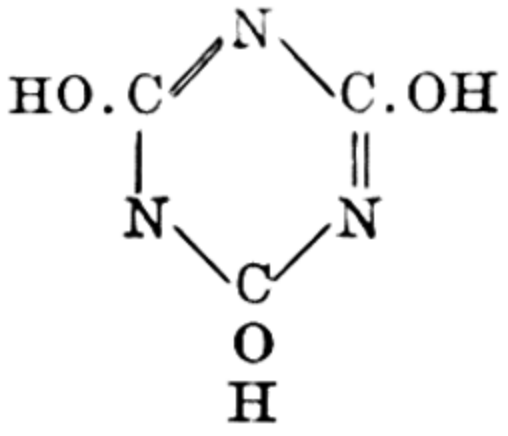
**579. Cyanic Acid and the Cyanates.**—Cyanic acid HOCN is prepared by heating cyanuric acid $(HOCN)_3$ in a stream of carbon dioxide and condensing the vapour in a freezing mixture. It may also be made by the action of phosphorus pentoxide on urea, $CO(NH_2)_2$.

Cyanic acid is a gas of pungent odour, which is easily liquefied in a freezing mixture. Its most conspicuous property is its *polymerisation* to cyanuric acid $(CHON)_3$,

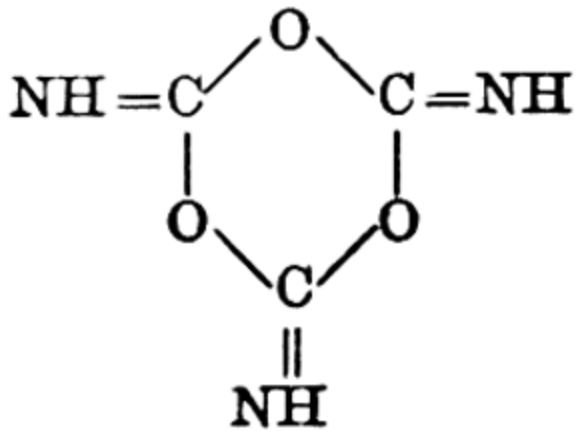
$$3HOCN = (HOCN)_3,$$

and also to cyamelide, a white compound also of formula $(HOCN)_3$.

Cyanic acid is a stronger acid than hydrocyanic acid. Its structure may be either $H - O - C \equiv N$ or $H - N = C = O$. Its polymers, cyanuric acid and cyamelide, are probably,




Cyanuric acid.




Cyamelide.

Potassium cyanate KCNO is made by the action of red lead on fused potassium cyanide,

$$4KCN + Pb_3O_4 = 4KCNO + 3Pb.$$

It is a white crystalline substance soluble in water. Ammonium cyanate $NH_4.CNO$ is of interest on account of its ready transformation to the isomeric urea $NH_2 - CO - NH_2$. This preparation, first performed by Wöhler in 1828, was the first example of the formation of an animal product from inorganic materials.

**580. Thiocyanic Acid and the Thiocyanates.**—Thiocyanic acid HCNS may be made by distilling potassium thiocyanate with dilute sulphuric acid at low temperature, drying the gas evolved and condensing it in a ∪-tube cooled in a freezing mixture. The liquid polymerises on standing.

Potassium thiocyanate KCNS is made by fusing potassium cyanide with sulphur. The product is dissolved in alcohol, which leaves behind potassium sulphate, etc., as an insoluble residue, and crystallised by evaporation.

Potassium thiocyanate is a crystalline salt extremely soluble in water.

The action of strong acids does not liberate thiocyanic acid, but other products, including oxides of carbon, carbonyl sulphide, sulphur, etc.

With ferric salts it forms a deep red solution, and this is a very sensitive test for ferric iron. The red compound is soluble in ether (§ 1166).

**580a. Oxycyanogen and Thiocyanogen.**—*Oxycyanogen* $(OCN)_2$ has been made by electrolysis of potassium cyanate or by action of iodine on silver cyanate in carbon tetrachloride solution

$$2AgOCN + I_2 = 2AgI + (OCN)_2.$$

It forms colourless crystals which melt at − 12° C. It has the odour of a halogen, is a strong oxidising agent and attacks metals without liberating hydrogen.

*Thiocyanogen* $(SCN)_2$ has been made by the action of bromine on lead thiocyanate in ethereal solution. It forms colourless crystals. Like oxycyanogen, it resembles a halogen.

*Selenocyanogen* has also been prepared.

Oxycyanogen is stable in solution up to 100° C., but thiocyanogen decomposes even below room temperature.

**580b. Cyanamide $NC.NH_2$.**—Cyanamide takes its chief importance from calcium cyanamide $CaCN_2$ which is sold as a fertiliser "Nitrolim," in quantities of about 1,000,000 tons yearly. It is manufactured by heating calcium carbide in an atmosphere of nitrogen at 800° to 1,000 °C.

$$CaC_2 + N_2 = CaCN_2 + C.$$

The crude product is ground and sold as a fertiliser. Its value as such is due to its formation of ammonium salts in presence of moisture, to a small extent directly, but chiefly *via* cyanamide and urea.

$$(CaCN_2 + 3H_2O = CaCO_3 + 2NH_3)$$
$$CaCN_2 + CO_2 + H_2O = CaCO_3 + NC.NH_2$$
$$NC.NH_2 + H_2O = CO(NH_2)_2$$

Urea

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3.$$

It also finds a use for making cyanides (§ 261).

*Cyanamide* $NC.NH_2$ is made by treating calcium cyanamide for many hours with 40 per cent. acetic acid and extracting the residue with ether.

It forms colourless deliquescent crystals, melting point 43°–44° C. It boils at 140° C., (19 mm.) It readily polymerises and also hydrolyses (*v.s.*). It acts as a very weak acid, forming salts such as $CaN.CN$, $Na_2N.CN$, etc.

**581. The Colour Reactions of Iron with Compounds of the Cyanogen Group.**—Iron forms very characteristic salts with ferrocyanic, ferricyanic and thiocyanic acids. These are used as a means of detecting and distinguishing ferrous and ferric salts and also as a means of detecting the above-mentioned acids. The tests and reactions are discussed in § 1171.

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## Combustion and Flame

**582. Nature of Combustion.**—Combustion in its widest sense may be regarded as a reaction taking place at a high temperature and producing enough heat to maintain the temperature of reaction.

Thus charcoal burns in air. Once it is heated to about 500° C. the charcoal combines with oxygen, according to the reaction

$$C + O_2 = CO_2 + 97 \text{ Cals.},$$

and the heat produced keeps the charcoal at a temperature at which the reaction continues without further external heat.

Copper, on the other hand, does not burn in air. When heated to 500° C. the reaction

$$2Cu + O_2 = 2CuO$$

takes place, but the heat produced by it is insufficient to keep the copper at a temperature at which the reaction will continue.

The combustion of non-volatile solids is flameless. If a flame is produced by a burning solid some gaseous product has been formed. Thus carbon, iron, ferrous oxide burn without a flame. On the other hand, phosphorus, sodium, magnesium, etc., are vaporised by the heat of combustion and their vapours burn with flames. With very few exceptions liquids do not themselves burn, but are volatilised to vapours which burn with a flame.

The investigation of the burning of gases resolves itself into the study of explosive mixtures and flame, a vexed subject which has been ably studied for many years by such eminent investigators as Dixon and Bone. Much light has been thrown by them on the problems of the mechanism of combustion, luminosity of flames, etc., but a good many points are still at issue.

**583. Flames.**—The combustion of solids and liquids gives rise to heat. The unburnt solid or the products of combustion are raised thereby to a temperature at which they emit both heat radiation and light radiation and, consequently, the process of combustion is accompanied by light.

The case of gases is not by any means as simple. If an ordinary colourless gas, such as air, is heated, nothing in the nature of a glow or light is produced even at the highest temperatures. Consequently the explanation of a flame as gas raised to such a high temperature that it radiates light is an inadequate one.

A flame is undoubtedly glowing gas, but the gas does not glow through the effect of temperature only but also by a manifestation of chemical energy.

Some flames contain solid particles, and the light given by these is

easily explained as due to the light radiated by the glowing solid. Examples of such flames are those of acetylene, coal-gas, magnesium. This explanation of the light given by flames is not by any means complete, for it does not explain the brilliant light given by the phosphorus flame (both phosphorus and its oxide are vapours at flame temperature), nor the very perceptible blue light given by the 'non-luminous' Bunsen flame, the flame of carbon disulphide, hydrogen sulphide, etc.

We may best elucidate the subject of flames by discussing several simple cases.

(1) The hydrogen flame. It might seem that nothing could be simpler than the burning of hydrogen in oxygen to form water,

$$2H_2 + O_2 = 2H_2O,$$

but in fact the mechanism is quite complex, and a complete book has been written on this reaction alone. Below 500° C. the reaction between the gases takes place only at solid surfaces, such as the walls of the vessel. At higher temperatures (540–590° C.) the reaction between the gases proceeds by a chain reaction. A hydrogen molecule combines with an oxygen molecule, forming a molecule of hydrogen peroxide,

$$(1)\ H_2 + O_2 = H_2O_2,$$

which then reacts with a molecule of hydrogen forming two

$$(2)\ H_2O_2 + H_2 = H_2O^* + H_2O$$

molecules of water. The energy liberated 'activates' one of the water molecules ($H_2O^*$), *i.e.*, gives it a greater amount of *internal* energy. The water molecule then activates an oxygen molecule, which, as a result of its extra energy, can combine with another hydrogen molecule, again forming hydrogen peroxide and restarting the cycle.

$$(3)\ H_2O^* + O_2 = H_2O + O_2^*.$$
$$(4)\ O_2^* + H_2 = H_2O_2.$$

In this way the reaction proceeds in a linear manner, a chain of water molecules marking its course. Chains of this kind have undoubtedly a real existence, for they have been photographed. The fact that hydrogen peroxide occurs in the products of combustion supports the theory, as does also a quantitative study of the speed of the reaction.

At temperatures above 590° C. both of the water molecules of

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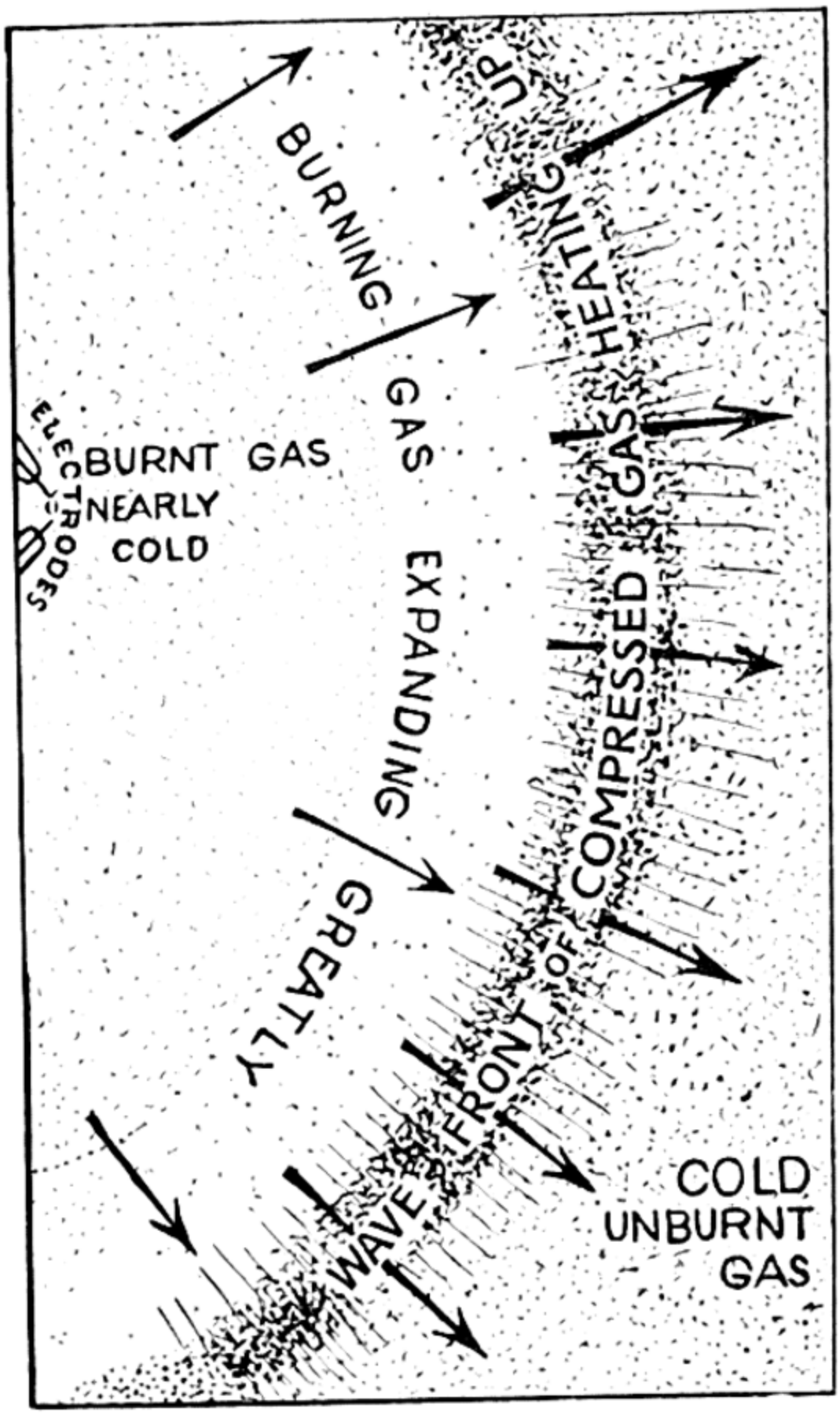


FIG. 110.—Explosion wave.

equation (2) may be activated; the chain then branches and forms a new chain, which itself forms further branches. This leads to a great and progressive increase in the speed of reaction and an explosion occurs. New phenomena then come into play. If a portion of the gas begins to burn explosively (as, for example, when ignited by a spark) the first portion of gas ignited reaches an immensely high temperature (*c.* 3,000° C.) and increases very greatly in volume as a result of the heat evolved. The expanding gas compresses the cold gas in contact with it just as in a sound wave. The explosion wave, however, differs from a sound wave in that the compressed gas of the moving wave itself explodes and thrusts the pressure wave forward with a velocity approximately equal to twice that of sound. Fig. 110 gives an idea of the nature of the explosion wave by which this type of combustion is propagated.

If hydrogen burns at the orifice of a jet the conditions are very different. In a *mixture* of hydrogen and oxygen the rate of explosion is regulated by the rate at which the explosion wave is travelling through the gas; but where hydrogen burns at a jet the determining factor is the rate at which oxygen can reach the burning gas. Combustion can, therefore, only take place where the air or oxygen meets the hydrogen and at this point a heated layer of gas, the flame, is formed. The maintenance of a flame in one spot and the typical shape of the flame are due to two factors. The combustion using up the hydrogen makes the flame tend always to travel downwards (just as a flame burns down a match-stick); the gas in the tube is, however, travelling upwards, most rapidly at the axis and very slowly at the edges. The speed of the gas as it travels upwards grows less as the gas spreads into the air, and at some point becomes equal to

the velocity of the flame travelling downwards, and the locus of these points gives the shape of the flame. If the velocity of the gas up the tube is too great the flame is blown out, *i.e.*, is carried upward more quickly than it can burn downwards.

A flame of pure hydrogen, burning in dust-free air, is invisible, but many gas flames, as of carbon monoxide, hydrogen sulphide, etc., give a blue light.

This blue light is not to be attributed to glowing particles of solid in the gas, for even if these were present they would not emit a blue light. The spectrum of the light is continuous, with ill-defined bands of greater intensity, and is quite different in character to that of a glowing metallic vapour, which gives a line spectrum.

**584. Bright Flames.**—A number of gases burn with flames of very great luminosity. These include the hydrocarbon gases (except methane), the vapours of many metals, phosphorus, phosphine, and the volatile hydrides of certain elements, *e.g.*, silicon hydride.

It was at one time thought that all bright flames contained white-hot particles of solid, but it is quite clear that some do contain these particles and that some do not. The flames of phosphorus and phosphine (*v. supra*) contain no solid and the light radiated by them is probably due to the same cause as that of the blue flames of carbon monoxide, etc. The reason for the luminosity of these flames is not at present clearly understood. It is certain, however, that the gases in a flame are ionised and that when the ions regain electrons and settle down to the normal state light is emitted, but this does not explain the very great differences in luminosity between individual types of flame. On the whole, dense or compressed gases give luminous flames, while light or rarefied gases have feebly luminous flames.

The flames of hydrocarbon gases are of far greater practical interest than any others, and the luminosity of these is certainly, for the most part, due to the presence of glowing solid carbon.

The candle flame and that of the Bunsen burner may be taken as typical.

A luminous hydrocarbon flame of this kind shows four distinct zones.

(1) A faintly luminous mantle surrounding the whole flame.

(2) A brightly luminous yellow area from which almost all the light comes.

(3) An inner cold hollow space containing unburnt gas.

(4) A ' dark-blue ' region at the base.

The process which gives rise to this structure is as follows :—

(I) In the case of the candle the heat of the flame vaporises the hydrocarbon on the wick, or in the case of the gas-burner the gas

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rises out of the jet. In either case, a hollow space (3), containing unburnt gas, is formed. This space is cold, as may be seen by stretching an iron wire across the flame. The wire glows where it traverses the outer part of the flame but remains dark where it

Candle flame Luminous Bunsen flame

FIG. 111.

FIG. 112.

crosses the centre. The space may be shown to be full of unburned gas by the simple process of drawing off a portion through a tube (Fig. 112).

(II) The *base* of this unburned area meets a full supply of uprising air and complete combustion takes place without separation of carbon. This process brings about the formation of the 'dark-blue' zone (4).

(III) The greater part of the gas or vapour is decomposed in such a way as to cause carbon to separate in minute particles. It used to be thought that this was due to the oxygen of the air combining with the hydrogen of the gas and liberating carbon,

$$C_2H_4 + O_2 = 2C + 2H_2O,$$

but experimental evidence shows that the preference is actually the other way, and that if any such action took place the reaction

$$C_2H_4 + 2O_2 = 2CO_2 + 2H_2$$

would be more likely. Bone and his co-workers have accumulated a good deal of evidence that combustion takes place by hydroxylation. Thus the burning of ethane in an insufficient supply of oxygen probably proceeds by the reactions :—

$$\underset{\text{ethane.}}{C_2H_6} \xrightarrow{O} \underset{\text{alcohol.}}{C_2H_5OH} \xrightarrow{O} \underset{\text{ethylidene glycol (unstable).}}{CH_3.CH(OH)_2} \xrightarrow{\text{heat}}$$

$$\rightarrow H_2O + \underset{\text{acetaldehyde.}}{CH_3.CHO} \xrightarrow{\text{heat}} CH_4 + CO$$
$$C + 2H_2O + CO \text{ etc.}$$

but may be a much more complex process.

The carbon when formed is heated to a high temperature

(*c.* 1,700° C.) and glows brightly with a yellowish-white light. Some flames (*e.g.*, that of coal-gas burning in chlorine) are red owing to their lower temperature.

In this luminous zone of the flame there is an insufficient supply of oxygen and a partial combustion takes place, becoming more complete as the gases pass upwards and outwards. Finally, the carbon

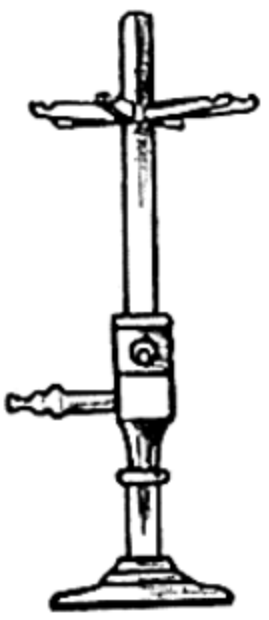

FIG. 113.—The original Bunsen burner (1855).

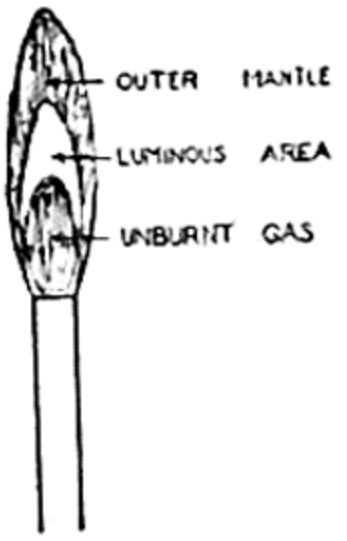


FIG. 114.

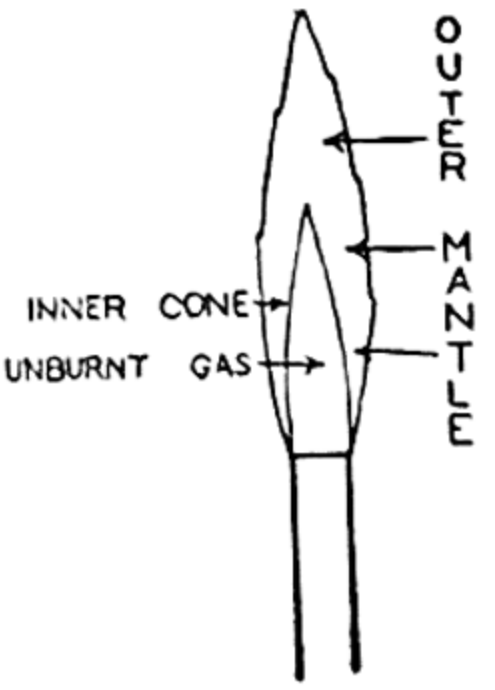


FIG. 115.—The Bunsen flame.

and other products of incomplete combustion come very close to the outer air, where there is a full supply of oxygen.

(IV) The carbon and products of incomplete combustion burn to carbon dioxide and water in the outer mantle. This complete combustion does not always occur. Where there is a very free supply of combustible the quantity of carbon, etc., is too great to be consumed by the available air supply and smoking occurs. The deposition of carbon from such a flame is increased by slowing down the combustion or by diminishing the air supply in any way as, for example, by placing a cold object in the flame.

**585. The Bunsen Burner.**—The incomplete combustion of a hydrocarbon flame is in every way undesirable if such a flame is to be used for heating purposes. The deposition of soot on heating surfaces diminishes the rate at which heat is conducted to them as well as making them dirty. Bunsen, in 1855, devised the Bunsen burner, an instrument so satisfactory that it has only been altered in minor details in eighty-five years. The gas-ring, gas-fire heating element, etc., all depend on the same principle.

In the Bunsen burner the gas, under the usual pressure of some 3 inches of water, issues from a jet and in injector fashion draws a supply of air through an air-port into a tube, where gas and air become mixed, the proportion in a normal Bunsen burner being about 1 : 2·5. The mixture burns at the top of the tube with a blue flame of simple structure. We may study with advantage the changes which take place in the luminous gas flame when air is

introduced into the gas. The first stage is a diminution of the yellow luminous area and a widening of the outer mantle (Fig. 114).

The addition of further air leads to the disappearance of the yellow luminous area.

Still further air being introduced, the hollow area of unburnt gas becomes converted into a definite blue luminous inner cone and the usual 'Bunsen flame' is produced. This consists of three definite regions :—

(1) The outer mantle.
(2) The more luminous inner cone.
(3) The hollow space containing unburnt gas.

The process of combustion in this type of flame is :—

(1) A vigorous combustion at the surface of the inner cone. Here the air contained in the gas mixture is burned.

(2) A less vigorous combustion of the excess of gas and products of combustion in the outer mantle.

The addition of still more air increases the velocity of combustion of the mixture and, consequently, makes the flame shorter and smaller and also hotter. The final result of the addition of further air is that gas burns downwards so rapidly that no space containing unburnt gas remains, and the flame passes down the tube and burns at the jet below. The burner is then said to have 'struck back.' The gas burns in the tube incompletely, and hydrocarbons, such as acetylene, are produced and escape unburned. This striking back can be avoided by placing at the top of the tube a diaphragm through which a flame will not pass. Such a diaphragm may be formed of several thicknesses of coarse wire gauze (Fisher burner), or of a deep nickel grid (Méker burner). A flame is then produced in which very rapid combustion occurs. Such a flame is considerably hotter than the Bunsen flame.

The logical conclusion would be to use a mixture of gas and air in the proportions required for perfect combustion (approximately 1 : 6). This has been done in the Bonecourt surface heaters, which are finding industrial uses, more particularly in the U.S.A. In these heaters a mixture of gas with enough air for complete combustion passes through a porous diaphragm of refractory material. Nearly all gas reactions are catalysed by solid surfaces and so a very rapid combustion takes place in the outermost layer of the porous material, raising it to a high temperature. This is probably the most efficient way of using coal-gas, but has not made great headway in this country, probably owing to a fear of explosion of the air-gas mixture.

# CHAPTER XVI

# SILICON, TIN AND LEAD AND THE REMAINING ELEMENTS OF GROUP IV

**586. Group IV. of the Periodic Table.**—Group IV. of the Periodic table is constituted as follows :—

| A Sub-Group | B Sub-Group. |
|---|---|
| | Carbon. |
| | Silicon. |
| Titanium. | |
| | Germanium. |
| Zirconium. | |
| | Tin. |
| Hafnium. | |
| | Lead. |
| Thorium. | |

The typical elements, carbon and silicon, bear a stronger resemblance to the B sub-group than to the A sub-group. The A sub-group is discussed in § 651.

**587. Typical Elements and B Sub-group.**—The elements carbon, silicon, germanium, tin and lead show a marked and instructive gradation of properties as we pass from the first to the last. There are, however, few properties common to these five elements, and there are no such resemblances between carbon and lead as we find between, say, lithium and cæsium.

The following common properties are to be noted :—

(1) All the elements of the group show a valency of four.

(2) All the elements have a hydride, $XH_4$ (exceedingly unstable in the case of tin and lead), an oxide with acidic characters, $XO_2$, a liquid tetrachloride, $XCl_4$, and organic ethyl derivatives such as $X(C_2H_5)_4$.

The gradation of properties is of interest and may, perhaps, be best expressed in the form of a table. As we pass from carbon to lead, there will be noted—

(1) a progressive increase in metallic character ;

(2) a progressive tendency towards the formation of compounds in which the elements are bivalent.

| | Carbon. | Silicon. | Germanium. | Tin. | Lead. |
|---|---|---|---|---|---|
| Physical properties of element. | Typically non metallic. | Typically non-metallic. | Metallic or metalloid. | Typically metallic. | Typically metallic. |
| Chemical reactions of element. | Attacked only by oxidising agents. Typical non-metal. | Similar to carbon. Attacked by hydrogen fluoride | More reactive than C or Si. Not attacked by acids other than oxidising agents. | Has the typical reactions of a metal except in its oxidation to an oxide by nitric acid. | Has the reactions of a typical metal. |
| Hydrides . | Very numerous and for the most part stable and unreactive. | Several hydrides: unstable: some spontaneously inflammable. | One hydride, $GeH_4$, unstable. | $SnH_4$ (?) decomposes spontaneously even at room temperature. | Existence of a hydride doubtful. |
| Bivalent compounds. | Probably none. | Probably none. | $GeCl_2$ is a very powerful reducing agent. | Strong reducing agents. | No reducing power. |
| Oxides . | All acidic or neutral. | Acidic or neutral. | Acidic and basic. | Acidic and basic. | Acidic and basic. |
| Halides . | Not ionised and very stable. | Not ionised, readily hydrolysed. | Not ionised. | Tetrahalides not ionised. Dihalides are ionisable salts. | Tetrahalides very unstable and are not ionised. Dihalides are ionised and typical salts. |
| Salts with oxyacids. | None. | None. | None. | Oxysalts of tetravalent tin are unstable. Divalent tin forms oxysalts. | Tetravalent lead forms a sulphate. Divalent lead forms stable oxysalts. |

**588. Atomic Structure of Typical Elements and Sub-group IV. B.**—The atoms of these elements are characterised by an outer layer of four valency electrons. The major groups of electrons can be subdivided into sub-groups and the outer four electrons in the atoms of these elements form two pairs.

| | Electrons in groups characterised by | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 quantum. | 2 quanta. | | 3 quanta. | | 4 quanta. | | 5 quanta. | | 6 quanta. | |
| | | $2_1$ | $2_2$ | $3_1$ | $3_2$ | $4_1$ | $4_2$ | $5_1$ | $5_2$ | $6_1$ | $6_2$ |
| Carbon . . | 2 | 2 | 2 | | | | | | | | |
| Silicon . . | 2 | 8 | | 2 | 2 | | | | | | |
| Germanium . | 2 | 8 | | 18 | | 2 | 2 | | | | |
| Tin. . . | 2 | 8 | | 18 | | 18 | | 2 | 2 | | |
| Lead . . | 2 | 8 | | 18 | | 32 | | 18 | | 2 | 2 |

In carbon and silicon all four are always used as valency electrons; in germanium nearly always; in tin either all four (stannic compounds) or only one pair (stannous compounds). In the tetravalent lead compounds again both pairs are used, while in the ordinary bivalent lead compounds only one pair is in use.

The pair of electrons which does not readily take part in chemical combination is called 'the inert pair.' Its influence is conspicuous in the elements thallium, lead and bismuth, and noticeable in the chemistry of indium, germanium, tin, antimony, sulphur, selenium, tellurium and iodine, all of which have a tendency to show a valency two units less than the maximum.

| Element. | Structure. Electrons of | | | Electrons available for valency purposes. | Actual Valency in Salts. |
|---|---|---|---|---|---|
| | 1–5 quanta. | $6_1$ | $6_2$ | | |
| Thallium . . | 78 | 2 | 1 | 3 | 1 and 3 |
| Lead . . | 78 | 2 | 2 | 4 | 2 |
| Bismuth . . | 78 | 2 | 3 | 5 | 3 |

## SILICON Si, 28·06

**589. Characteristics of Silicon.**—The element silicon is, after oxygen, the most abundant in the earth's crust. The greater part of the igneous rocks consist of silicates—in particular those of magnesium, aluminium, potassium and iron—combined to form various double silicates and complex mixtures. The oxide of silicon, $SiO_2$, abounds as quartz, flint, sand, etc. The chemistry of silicon differs from that of carbon mainly in that silicon does not readily form long chains of linked atoms, although chains of three

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or four atoms are not uncommon. It appears, rather, that silicon forms linkages of the type .. Si—O—Si—O—Si—O—, and such linkages are instrumental in building up such complex compounds as the mineral silicates, glasses, etc.

**590. Preparation of Silicon.**—Silicon, it is said, exists in two allotropic forms, but it is very doubtful if these are true allotropes. They are known as amorphous silicon and adamantine[1] silicon. Graphitoidal silicon is described by some authors, but has no separate identity.

*Amorphous silicon*, the usual form, is best prepared by heating magnesium or aluminium powder with silica, the very violent action being moderated by the presence of magnesium oxide,

$$2Mg + SiO_2 = 2MgO + Si.$$

The product is heated first with dilute hydrochloric acid and finally with hydrofluoric acid. Silicon remains behind as a maroon-coloured powder.

*Adamantine silicon* is best made by the action of aluminium on potassium silicofluoride,

$$4Al + 3K_2SiF_6 = 4AlF_3 + 6KF + 3Si.$$

Extraction with dilute acids and finally dilute hydrofluoric acid (1 : 1) yields the pure silicon. When pure it forms small yellow transparent crystals.

**591. Properties of Silicon.**—Like the forms of carbon, the forms of silicon differ in chemical behaviour as well as in physical properties, the 'amorphous' form, as with carbon, being the most reactive. It seems likely, however, that the differences between them are only due to differences in surface and particle size and that amorphous silicon is only a finely divided crystalline silicon.

*Amorphous silicon* is a brown or reddish powder of sp. gr. 2·36. It fuses at a high temperature.

Chemically it is fairly reactive, burning in oxygen at or below a red heat,

$$Si + O_2 = SiO_2.$$

It reacts with fluorine at the ordinary temperatures, and with chlorine and bromine at a low red heat,

$$Si + 2Cl_2 = SiCl_4.$$

It also combines with sulphur and nitrogen. Silicon reacts with boiling water or steam,

$$Si + 2H_2O = SiO_2 + 2H_2.$$

*Adamantine silicon* forms pale yellow crystals of octahedral type, which have curved faces capable, like those of the diamond, of cutting glass.

Adamantine silicon burns at 400° C. in oxygen, but less easily than the 'amorphous' form.

Silicon finds a use in the manufacture of silicon steel and silicon bronze.

**592. Atomic Weight of Silicon.**—The approximate atomic weight of silicon is evidently 28, as is shown by the vapour densities of numerous volatile compounds. Its obvious analogy to carbon places it clearly in the fourth

[1] *Adamas*, Lat. diamond.

group of the Periodic table and also indicates this atomic weight. Dulong and Petit's rule also confirms this at temperatures above 200° C.

The equivalent is nearly 7 and the valency is accordingly 4. The exact determination of the atomic weight has been best carried out by dissolving a known weight of a silicon halide, $SiCl_4$, $SiBr_4$, in water and determining the weight of silica produced on ignition of the residue,

$$SiCl_4 + 4H_2O = Si(OH)_4 + 4HCl$$
$$Si(OH)_4 = SiO_2 + 2H_2O.$$

**593. Silicon Hydrides or Silanes.**—Several of these exist and are named after the corresponding carbon compounds,

| | |
|---|---|
| Silico-methane . . . . | $SiH_4$ |
| Silico-ethane . . . . | $Si_2H_6$ |
| Silico-ethylene . . . . | $Si_2H_4$ |
| Silico-acetylene . . . . | $(Si_2H_2)n$ |

have all been described.

**594. Silicon Hydride, Monosilane, Silicomethane,** $SiH_4$, is made by the action of hydrochloric acid on magnesium silicide, which latter may be made by heating magnesium powder with a suitable proportion of sand,

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$$

The gas is mixed with some 95 per cent. of hydrogen and the pure gas can be obtained by condensing the silico-methane with liquid air. The hydrides $Si_2H_6$, $Si_3H_8$, etc., are formed at the same time in small quantity and have been obtained by fractionating the liquefied gas.

Silicomethane is a colourless gas and, when impure, is spontaneously inflammable. It burns with a bright flame.

$$SiH_4 + 2O_2 = SiO_2 + 2H_2O.$$

### Oxides of Silicon

**595. Silicon Monoxide SiO** has been prepared by reduction of silica in the electric furnace. It behaves very much like a mixture of silicon and silica but seems to be a chemical individual.

**596. Silica, Silicon Dioxide, Silicic Anhydride, $SiO_2$,** is a very common mineral. It is found in nature in a pure crystalline condition as *quartz* and as *tridymite* (*v. infra*) and with various impurities as *chalcedony*, *hornstone*, *jasper*. *Opal* is an amorphous form of silica. *Flint* is also a less pure form of amorphous silica.

*Kieselguhr* consists of the fossil shells of the minute plants known as diatoms, and is a very porous and fairly pure form of silica.

Sand may be derived from many different sources, but usually consists of silica in a more or less pure condition. The purest form of silica is *rock crystal* or transparent quartz.

Silica may be prepared artificially in several ways.

(1) Silicon burns, forming silica,

$$Si + O_2 = SiO_2.$$

(2) Silicates may be decomposed by acids, yielding silicic acid, which when ignited gives silica,

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$$
$$H_2SiO_3 = SiO_2 + H_2O.$$

(3) Silicon fluoride is decomposed by water, forming silicic acid, which may be filtered off and ignited as above,

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6$$
$$H_4SiO_4 = SiO_2 + 2H_2O.$$

**597. Properties of Silica.**—Silica exists in four forms—

(1) Hexagonal crystalline silica—quartz (Plate XII).
(2) Hexagonal plates—tridymite.
(3) Cristobalite.
(4) Fused silica or quartz-glass.

Quartz and quartz glass are transparent colourless solids. When heated slowly crystalline quartz changes at about 870° C. to another crystalline form, *tridymite*, which at about 1,470° C. changes into a third form, *cristobalite*. Above this temperature it fuses to a liquid which solidifies to a clear glass, fused silica. The specific gravity of quartz is about 2·65 and that of quartz glass is 2·21. Silica is remarkably hard. It scratches glass but is itself scratched and cut by the diamond. Silica is remarkable for its extremely low coefficient of expansion. Fused silica has a coefficient of only $5 \times 10^{-7}$, while that of ordinary glass is *c.* $9 \times 10^{-6}$. This property gives one of its chief uses to fused silica. The cracking of glass apparatus by sudden heating or cooling is due, of course, to its low conductivity, which causes irregular expansion or contraction. The expansion of fused quartz being negligible, it will not crack even if plunged when red-hot into cold water. Fused silica is therefore a valuable material for many purposes. It has been used to construct laboratory apparatus and condensers for acids, evaporating pans, etc., for industrial purposes. Its disadvantage is its high price. The material is cheap enough, but the very high temperature (*c.* 1,600° C.) at which it has to be worked causes the difficulties in its manufacture.

Fused quartz can be drawn into threads of inconceivable tenuity, which are yet of considerable strength. Threads can be drawn which are quite invisible to the naked eye (·0005 cm. diameter) and will support a weight of a couple of grams. These threads, being elastic, are very valuable for the construction of physical apparatus.

Silica is slightly soluble in water, particularly when heated under pressure to temperatures of 110° C. and over.

Silica is very resistant to chemical action. It is, however, an acidic oxide, and is attacked by alkalis, forming silicates,

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O.$$

Metallic oxides do the same at a higher temperature (*v.* section on Glass).

$$PbO + SiO_2 = PbSiO_3.$$

Hence silica apparatus should not be used for concentrated alkalis or for heating metallic oxides.

Silica is attacked by hydrofluoric acid, yielding silicon fluoride (*q.v.*),

$$SiO_2 + 2H_2F_2 = SiF_4 + 2H_2O.$$

Silica finds numerous uses in industry.

Rock crystal is used as a gem and also for lenses, watch glasses, etc., which have the advantage of being unscratched in use.

Various ornamental forms, such as jasper and chalcedony, have been used as ornamental stones.

Flint was the subject of the world's earliest industry. Its use for flint implements depends on its peculiar fracture and its hardness.

Sand, of course, finds numerous uses in building, cement work, the manufacture of artificial stone, the manufacture of glass and glazes, water filtration, etc.

Kieselguhr is used for some of the above purposes and also for making dynamite (nitroglycerine absorbed in kieselguhr). It is also employed as a polishing powder and for numerous other purposes.

**598. Silicic Acids.**—The silicic acids are somewhat indefinite compounds, and it is doubtful how many of them actually exist.

| | |
|---|---|
| Orthosilicic acid . . . . | $H_4SiO_4$ |
| Metasilicic acid . . . . | $H_2SiO_3$ |

appear to be definite compounds. The empirical formula of the first is probably $Si(OH)_4$ and of the second $SiO(OH)_2$, but in all probability they are highly polymerised and the actual formulæ are $(H_4SiO_4)_n$ and $(H_2SiO_3)_n$.

Silicates exist derived from a number of other silicic acids. These are discussed on pp. 463, 464.

*Orthosilicic acid* is said to be obtained when silicon fluoride is passed into water and the gelatinous silica obtained is washed with ether and dried between filter papers,

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + H_4SiO_4.$$

It is a white powder.

*Metasilicic acid* is prepared by dehydrating the gelatinous silicic acid obtained by the action of acids upon sodium silicate with 90 per cent. alcohol.

*Silicic Acid Gels and Sols.*—When sodium silicate solution is heated to 100° C. and mixed with hydrochloric acid a gelatinous precipitate, silica gel, $SiO_2nH_2O$, is obtained. If, on the other hand, 100 c.c. of cold diluted hydrochloric acid (equal volumes concentrated acid and water) are added to 200 c.c. of cold ' water-glass ' solution (*c.* 30 per cent. $Na_2SiO_3$) a colloidal solution or sol of silicic acid (§ 91) is formed. This may be freed from sodium chloride by *dialysing* it. A purse-like bag of parchment paper is filled with the mixture and surrounded by running water as illustrated in Fig. 116. The sodium ions and chloride ions pass through the paper and are carried away while the colloidal silicic acid remains behind as a colourless and tasteless liquid. Its molecular weight is very high and its molecules are evidently very complex.

Silica gel has a remarkable power of absorbing moisture. Its use for drying the blast used in the smelting of iron is mentioned on p. 754. It has also the power of adsorbing many substances from

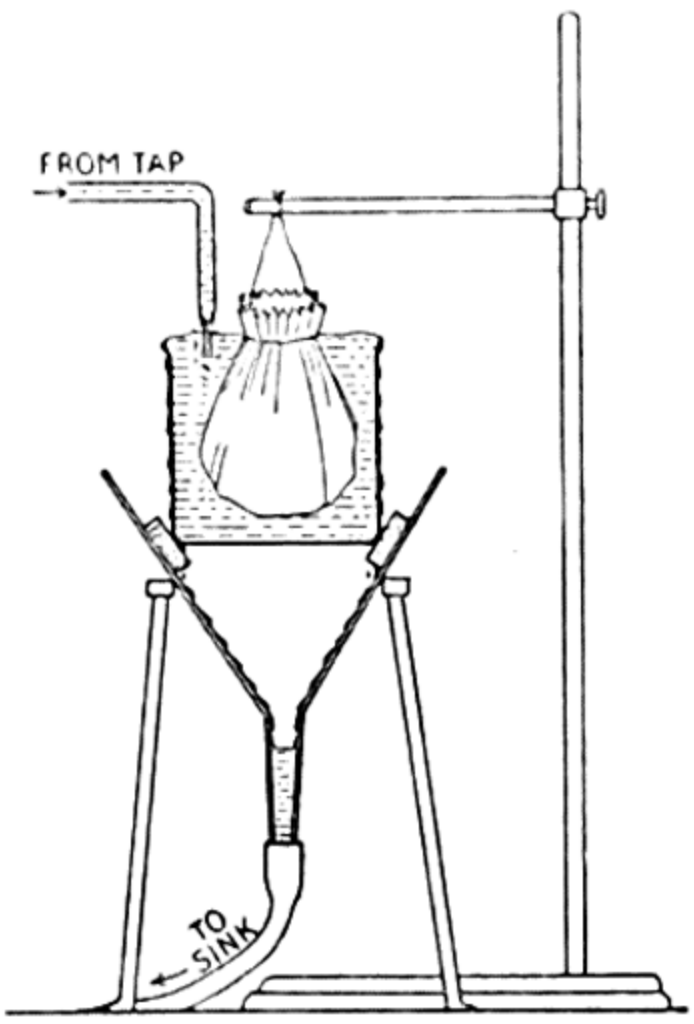


FIG. 116.—Purification of colloidal silica acid.

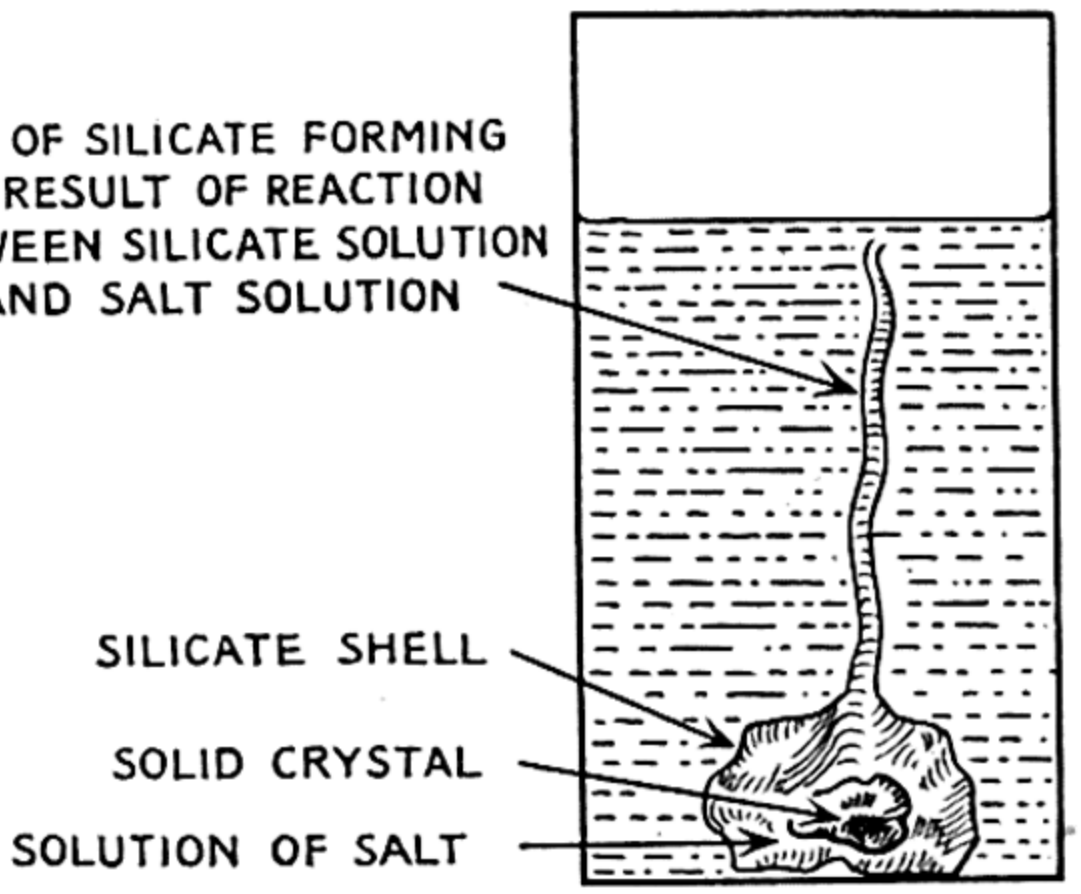


FIG. 117.—Production of silicate growths.

solution and has found some uses in removal of sulphur compounds from petroleum.

Other complex acids of silicon are known and are named after their carbon analogues. Silico-oxalic acid (HO.O.Si — SiO.OH) and Silico-mesoxalic acid $(SiOOH.Si(OH)_2.SiOOH)x$ are unstable and explosive.

**599. The Silicates.**—Sodium silicate is an article of commerce and is sold in concentrated solution as ' water-glass.' It is made by

fusing white sand with half its weight of soda. The glassy product is broken up and dissolved by long boiling with water under pressure. Its solutions react strongly alkaline (§ 121).

The silicates of the metals other than the alkali metals are insoluble in water. They may be prepared either by fusing metallic oxides with silica,

$$PbO + SiO_2 = PbSiO_3,$$

or by mixing a solution of sodium silicate with a solution of a metallic salt.

The remarkable 'silica-garden' (Fig 117, Plate XIII.) is made by preparing a solution of sodium silicate (density, 1·1) and filtering it, if necessary. In this solution are placed crystals of various salts, manganese chloride, cobalt nitrate, ferrous sulphate, copper sulphate being suitable. These crystals within a few hours become covered with long growths of fantastic shape consisting of hollow tubes of the solid silicate. The process of growth is probably as follows: Round the crystal is formed a shell of the silicate, colloidal and semipermeable (*v.* § 56). Within this is a strong solution of the salt—outside a weak solution of the silicate; hence water will pass through the shell and the osmotic pressure will burst it. As soon as it bursts the solution of the salt escapes but at once reacts with the silicate solution and thus builds up a further projection of the silicate. This again bursts and a further projection is built up and so on.

The metallic silicates are mainly of interest on account of their occurrence as minerals and their use in the manufacture of pottery and glass.

The igneous rocks consist for the most part of mixtures of silicates. We may take as examples some of the commonest minerals of which rocks are built up.

| | |
|---|---|
| Augite . . | Calcium magnesium silicate. |
| Felspar . . | Potassium aluminium silicate. |
| Hornblende . | Magnesium iron calcium silicate. |
| Kaolin, china clay, | Hydrated aluminium silicate. |
| Mica [1] . . | Hydrated potassium aluminium silicate. |
| Serpentine . . | Hydrated magnesium ferrous silicate. |
| Talc . . . | Hydrated magnesium silicate. |

Such crystalline rocks as granite, basalt, syenite, etc., are mixtures of these silicates which have cooled slowly, while glassy rocks, such as sanidine, obsidian, etc., are mixtures of silicates which have cooled very swiftly without time to crystallise.

**599a. Structure of Silicates.**—The difficulty of obtaining these silicates in a pure condition and the impossibility of directly determining their molecular weights has led to some very complex formulæ being given; the development of the technique of examining their structure by X-ray analysis, due chiefly to Bragg and his co-workers, has enabled their formulæ to be more certainly known.

[1] Several varieties exist of different composition.

Some are orthosilicates, such as olivine (Mg, Fe)$_2SiO_4$[1] and willemite $Zn_2SiO_4$. Others are meta-silicates, *e.g.*, diopside $CaMg(SiO_3)_2$. Others are derived from a hypothetical octosilicic acid $H_{16}(SiO_3)_8$; of these tremolite $H_2Ca_2Mg_5(SiO_3)_8$ may afford an example. The alumino-silicates, such as cyanite, sillimanite and andalusite, all $Al_2SiO_5$, and beryl $Be_3Al_2Si_6O_{18}$, are of a different type. Finally, the garnets of the type $M''_3.M'''_2(SiO_4)_3$, of which pyrope $Mg_3Al_2(SiO_4)_3$ is an example, form a large class.

A detailed study of the structures of these molecules is much beyond the scope of this book; suffice it to say that the hardness and insolubility of the silicates is due to their being giant molecules (§ 103) in which the whole mass is bound together by chemical linkage.

Thus olivine is not simple magnesium orthosilicate $Mg_2(SiO_4)$ (the iron is neglected for the moment), but a vast molecule $[Mg_2(SiO_4)]_n$ extending to the limits of the crystal, $n$ being of the order of $10^{20}$ or more.

Every oxygen atom is linked to one silicon atom and to three magnesium atoms, each of which is co-ordinated (§ 155) to six oxygen atoms in all. Fig. 118 gives some idea of the structure.

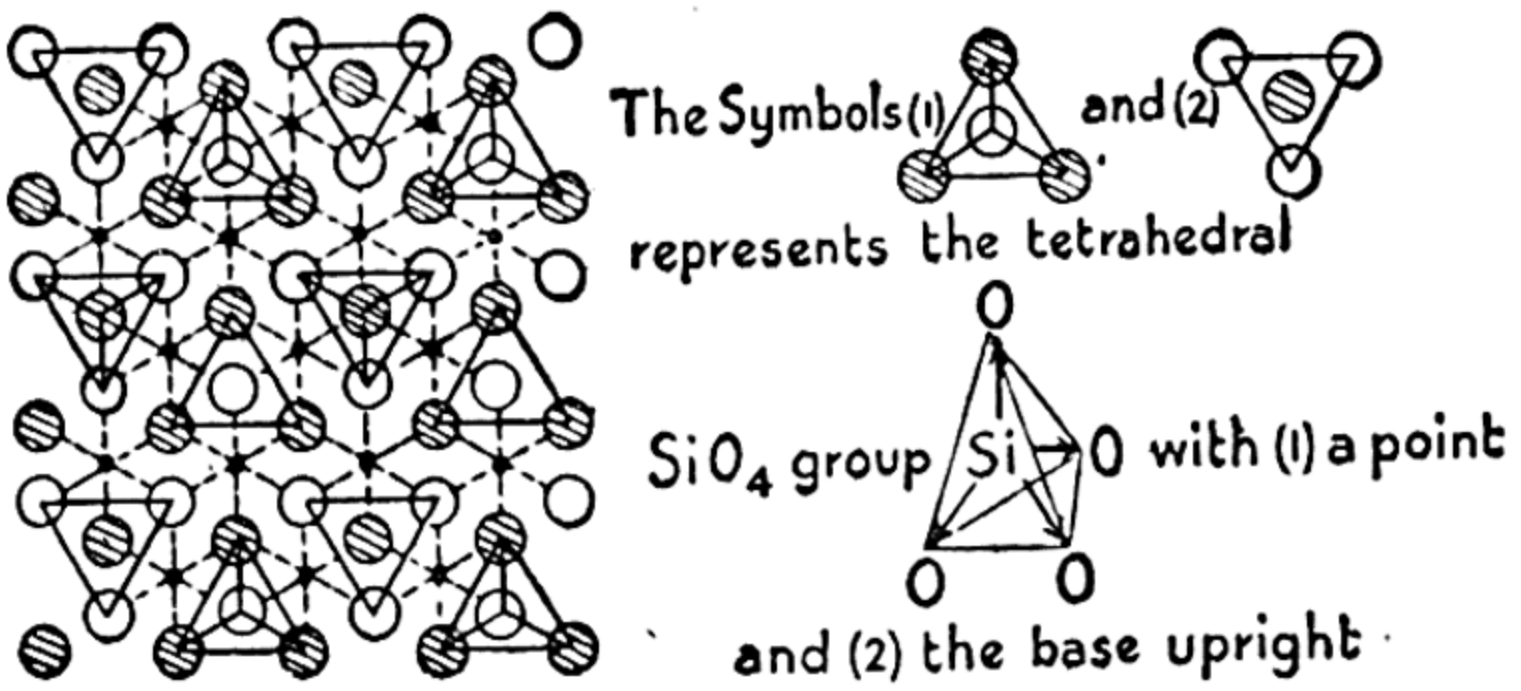


FIG. 118.—Projection of structure of olivine $(Mg_2SiO_4)_n$. The magnesium atoms are represented as black circles ●. The open circles ○ represent oxygen atoms above the plane of the paper. The shaded circles ◍ are oxygen atoms below the plane of the paper. The silicon atoms (not shown) lie at the centres of the tetrahedra of oxygen atoms represented above. The six co-ordinate linkages to the magnesium atoms bind the whole into a giant molecule and are represented by dotted lines. The structure extends indefinitely both vertically and horizontally. (Adapted from Bragg: *Structure of Silicates.*)

The orthosilicates, such as olivine, are exceptional as having separate $SiO_4$ groups in which an oxygen atom belongs only to a single silicon atom. In the metasilicates, *e.g.*, $X''_2(SiO_3)_2$ chains of silicon and oxygen atoms occur. Thus in pyroxene, of which the simplest formula is $MgCa(SiO_3)_2$, chains of the type shown in Fig. 119 are found. The oxygen atoms are further co-ordinated to magnesium and calcium atoms which, themselves linking to more oxygen atoms, bind the whole into a compact giant molecule.

[1] (Mg, Fe) means that magnesium and ferrous iron may occur in varying proportions replacing each other atom by atom.

The total elucidation of the structure of a silicate molecule is naturally very laborious and not easy to grasp—at least without the habit of thinking in terms of 3-dimensional models. It is perhaps sufficient if the student grasps the general principle of tetrahedra, composed of silicon atoms at the centre

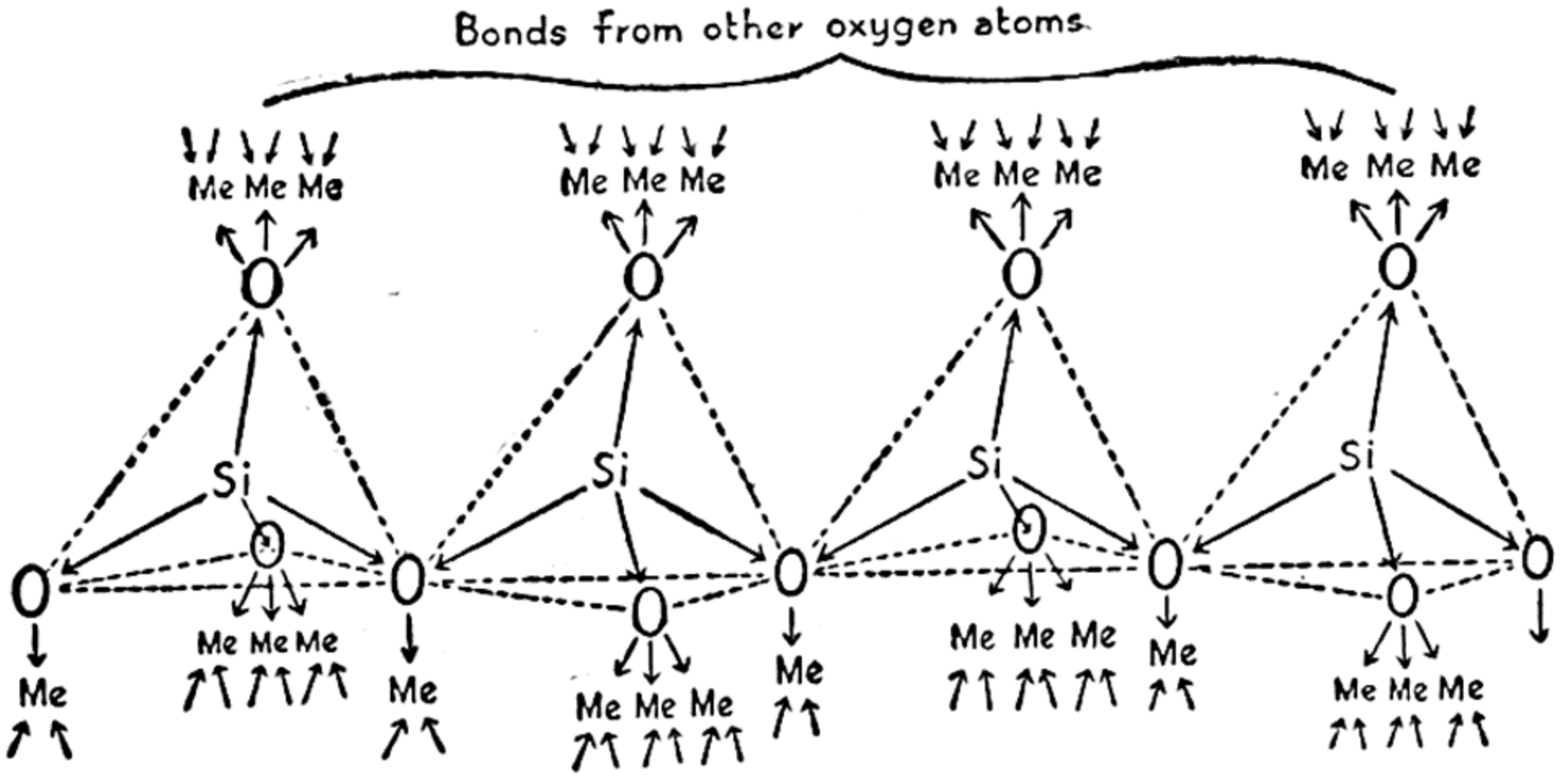


FIG. 119.—A chain of silicon and oxygen atoms as found in metasilicates $MeSiO_3$.

and oxygen atoms at the corners, linked by co-ordination to metallic atoms and to each other.

**599b. Ultramarines.**—The interesting and commercially very important blue pigment ultramarine is a complex silicate containing sulphur. It is made by roasting an intimate mixture of china clay and sodium sulphate with some soda, carbon and sulphur. It has a fine pure blue colour and is the most important blue pigment. There are numerous ultramarines, but the formula of a typical one is $Na_8Al_6(Si_4O_6).2Na_2SO_4$. The structure has been fairly clearly worked out as a sort of honeycomb of cells whose walls are a network of silicon, aluminium and oxygen atoms. The sodium ions cling to the walls of each "cell," and in each cell is an ionised group such as $NaSO_4'$. There is very good evidence for this or a closely related structure.

The study of these giant molecules of solids is opening up a new department of chemistry quite as different from organic chemistry and the inorganic chemistry of recent years as these are from each other.

Clay (§ 489) is of variable composition and is a heterogeneous mixture of particles of silicates, quartz, felspar, mica, etc., bound together by a sticky 'clay substance,' which is an aluminium silicate roughly of the formula $Al_2Si_2O_7.2H_2O$.

**600. Glasses.**—A glass is really a physical term, meaning a liquid *super-cooled* to such an extent that it has become apparently solid.

The term "glass," however, is generally applied to a fused mixture of two or more silicates. Such mixtures, if the composition is controlled appropriately, do not crystallise when cooled after fusing

and so form glasses. A glass is characterised by the fact that it has no definite melting point or crystalline character and when its temperature is raised it passes imperceptibly into a viscous liquid without showing any precise temperature point which could be taken as the melting point. Commercial glass consists essentially of a mixture of the silicates of sodium and calcium together with an excess of silica. This type of glass, used, for instance, for windows, has a composition approximating—

| | |
|---|---|
| $SiO_2$ | 70% |
| $CaO$ | 15% |
| $Na_2O$ | 15% |

This same composition is used for the manufacture of tubing for ordinary laboratory purposes but the modern "hard" glass used for chemical apparatus, i.e. Hysil or Pyrex, consists of a higher proportion of silica with some 15% of boric oxide, and a smaller amount of sodium oxide. For decorative tableware, it is general practice to use a lead-potash-silicate, since such a glass has a higher refractive index and, therefore, a brilliant appearance. The freedom of any glass from colour depends primarily on the lowness of the amount of iron oxide present as an impurity and this, in turn, depends on the purity of the sand used in its manufacture, since the other constituents can be obtained reasonably iron-free. Coloured glasses depend either on the addition of oxides which are capable of forming coloured silicates, e.g. of iron, manganese, copper or cobalt, or the addition of such materials as cuprous oxide, gold salts etc., which are capable of becoming dispersed in particles of a controlled size and form, in effect, a colloidal suspension in the glass matrix.

Glass is made by fusing together :—

(1) *Silica.*—Sand is used as a source of silica ; it must be free from iron oxide if colourless glass is required.

(2) *Alkali.*—Sodium carbonate or sulphate is employed ; or if a potash glass is wanted, potassium carbonate is used.

(3) *Lime.*—Chalk or limestone or lime itself is used.

A typical ' charge ' for making a batch of window-glass might be : sand 100 parts, sodium sulphate 32 parts, chalk 45 parts, coke 2 parts, to which is added a varying amount of *cullet* or broken glass.

Glass-making furnaces are of two main types. The first is the pot furnace in which a number of pots, built of selected clays, and heated in a furnace of a recuperative or regenerative type in order to give the high temperatures, 1300° C.–1450° C., required. Such furnaces are nowadays only used for the manufacture of

specialised types of glass. For commercial production of glass required in large quantities, such as for bottles, or window glass, "tank" furnaces are used. These consist of a large chamber built of refractory blocks capable of holding anything up to 1,000 tons of molten glass and heated by producer gas flames with a regenerative system to enable the necessary high temperatures to be reached.

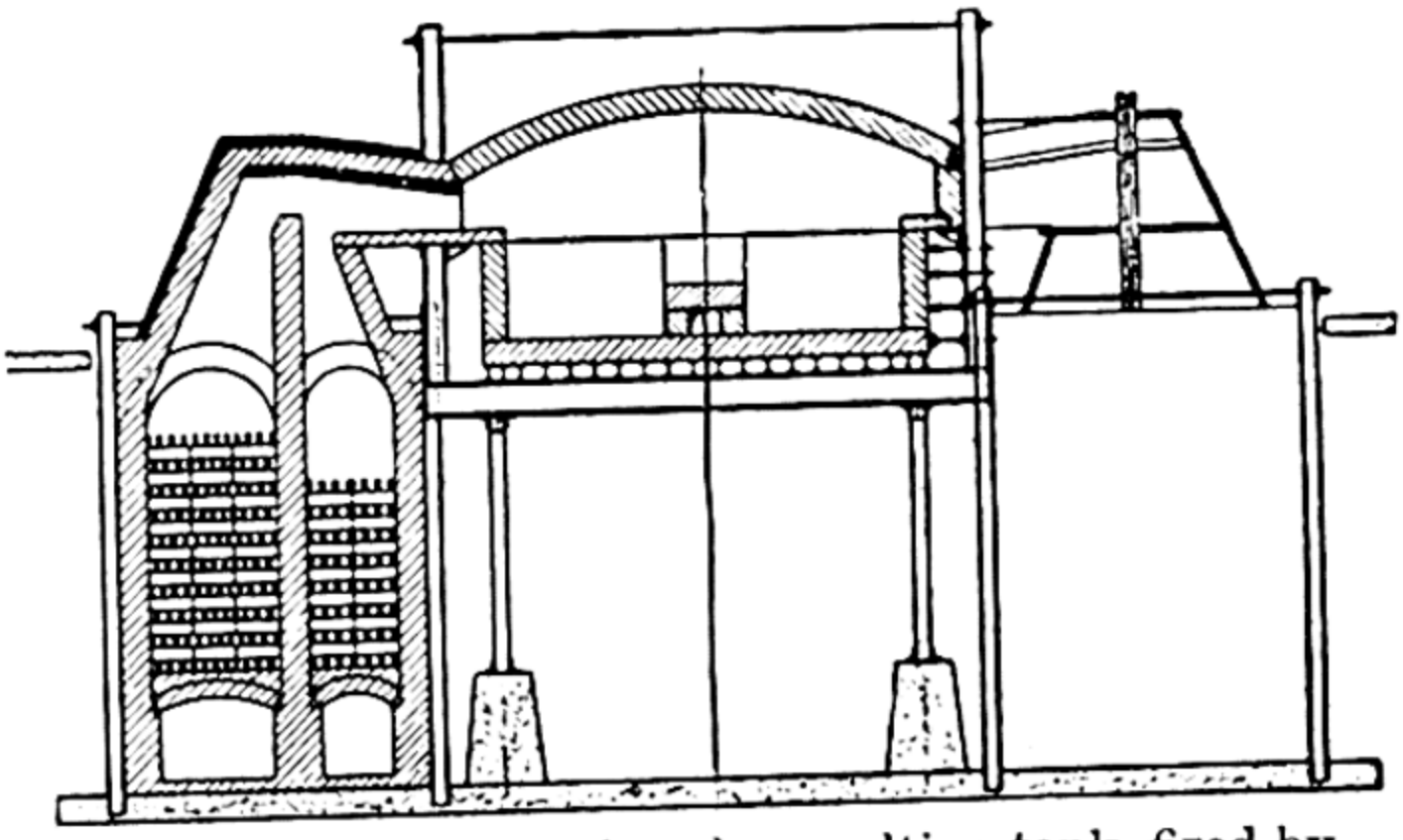

FIG. 121.—Regenerative glass melting tank, fired by producer gas (see pp. 429, 753).

Many methods of manipulation can be employed according to the type and shape of the article to be produced. The essential problem in the manufacture is the use of a temperature sufficiently high and a time sufficiently long to allow the gases formed by the reactions to escape and so enable the glass to be free from small gas bubbles.

*Pottery and China.*—Pottery and china are produced by heating clay to a high temperature and then coating it with a *glaze* and melting this to a thin glassy coating. The hardening of clay on firing depends first on the dehydrating of the aluminium silicate, which gives the 'sticky' character to it. This takes place at about 550° C. At higher temperatures some of the silicates contained in the clay actually melt and bind the remainder of its constituents into a stone-like or vitreous mass (§ 489).

The glazes applied to the surface of pottery are simply glasses of such composition that they are easily fusible and also have the same coefficient of expansion as the clay beneath. Neglect of this precaution causes the glaze to flake off. The quality of the porcelain or earthenware depends on the type of clay used.

**601. Silicon Halides.**—The most important of these are—

| | |
|---|---|
| Silicon fluoride . . . . . | $SiF_4$ |
| Silicon tetrachloride . . . . | $SiCl_4$ |

There also exist another fluoride $Si_2F_6$, other chlorides, $Si_2Cl_6$, $Si_3Cl_8$, $SiHCl_3$, corresponding to the various halides of carbon usually studied in organic chemistry. Many silicon bromides and iodides, including $SiBr_4$, $Si_2Br_6$, $SiHBr_3$, $SiI_4$, $Si_2I_6$, $SiHI_3$ have been described. A large number of silicon oxychlorides, $Si_2OCl_6$, etc., exist.

**602. Silicon Fluoride $SiF_4$.**—Silicon fluoride is made by the action of hydrofluoric acid upon a silicate or silica. The most convenient way of preparing the gas is to mix one part of fine sand or powdered glass with one part of powdered calcium fluoride and heat this with six parts of concentrated sulphuric acid. A glass flask may be used and, though it will be attacked, it will last out several experiments. The gas may be collected over mercury,

$$CaF_2 + H_2SO_4 = CaSO_4 + H_2F_2$$
$$2H_2F_2 + SiO_2 = SiF_4 + 2H_2O.$$

Silicon fluoride is a colourless gas with a suffocating odour. It does not burn. Its most striking property is its decomposition into gelatinous silica when passed into water,

$$3SiF_4 + 4H_2O = SiO_2.2H_2O + 2H_2SiF_6.$$

Gelatinous silicic acid is precipitated and a new acid, *hydrofluosilicic* acid, goes into solution.

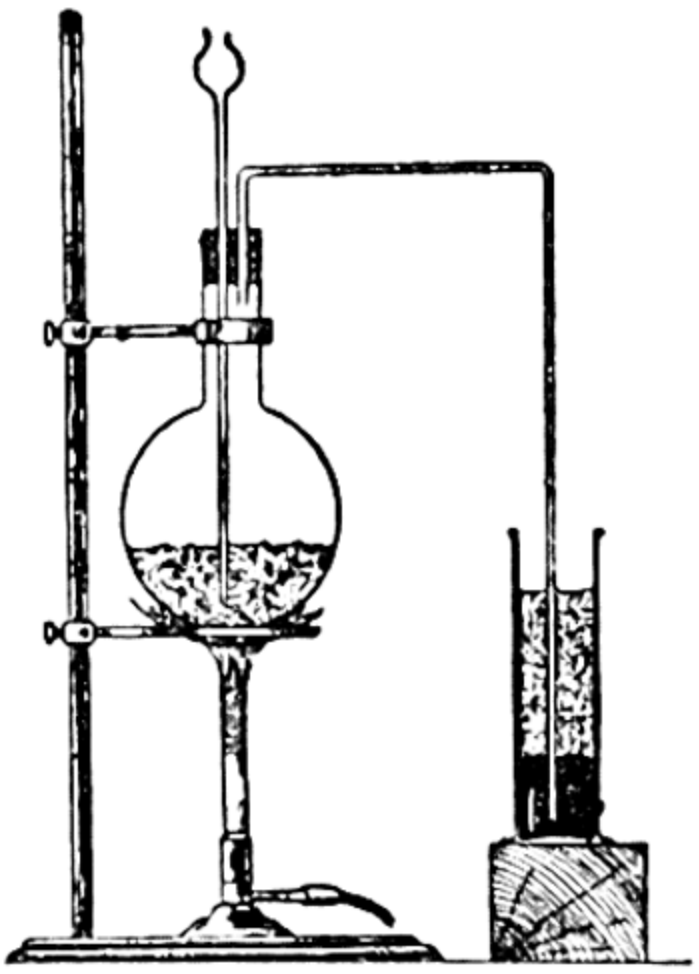

FIG. 122.—Preparation of hydrofluosilicic acid.

This property affords an excellent test for a silicate (and for a fluoride). If a silicate is to be tested for, it is mixed with calcium fluoride in a leaden or platinum crucible[1] and sulphuric acid added. The mixture is warmed and a drop of water hung on a glass rod is suspended in the vapours evolved. If silicates are present the rod will become coated with gelatinous silica.

Alkalis decompose the gas, forming silicates, fluorides and fluosilicates.

**603. Hydrofluosilicic acid $H_2SiF_6$** is prepared by passing silicon fluoride into water. The tube conveying the gas is best led under mercury as in the figure, for otherwise it becomes choked with gelatinous silica. A glass vessel may be used. After some time the hydrofluosilicic acid is filtered off and evaporated at a low temperature.

The concentrated solution of the acid is a fuming liquid. When evaporated to dryness it breaks up into hydrogen fluoride and silicon fluoride,

$$H_2SiF_6 = H_2F_2 + SiF_4.$$

[1] Glass and porcelain are inadmissible, being composed of silicates.

Its salts, the silicofluorides (fluosilicates), are of some slight importance. Potassium silicofluoride is but sparingly soluble and hydrofluosilicic acid is sometimes used as a precipitation reagent for potassium. Perchloric acid is, however, preferable. The silicofluorides have been used as disinfectants and food preservatives.

**604. Silicon Tetrachloride $SiCl_4$.**—This substance is made by heating silicon or magnesium silicide in a current of chlorine,

$$Si + 2Cl_2 = SiCl_4.$$

It forms a colourless liquid of B.P. 57° C. Like most of the chlorides of the non-metals it is decomposed by water; hydrochloric acid and silicic acids result,

$$SiCl_4 + 3H_2O = H_2SiO_3 + 4HCl.$$

Potassium metal decomposes its vapour, and this has been used as a means of preparing the element silicon,

$$4K + SiCl_4 = Si + 4KCl.$$

**605. Silicon Carbide SiC,** commonly known by the trade-name *Carborundum*, is a valuable abrasive. It is made by heating a mixture of carbon and silica in an electric furnace. A firebrick furnace about 16 × 5 × 5 feet has at each end an electrode consisting of some sixty large carbon rods 30″ long and 3″ in diameter. The furnace contains a charge of coke and sand, with sawdust and a little salt. A central core, joining the electrodes, is formed of pieces of coke. A current of 165 volts and 1,700 amperes passes at first. The current passing through the coke core forms arcs between the pieces of coke, and the temperature rapidly rises. The current passing rises to 6,000 amperes as the furnace heats up. The reaction

$$SiO_2 + 3C = SiC + 2CO$$

takes place. The carbon monoxide burns above the furnace. The silicon carbide is dug out, ground and graded into powders of different degrees of fineness.

Silicon carbide forms hexagonal crystals, colourless when pure, but normally dark-coloured, having a brilliant iridescent lustre. It is infusible, but decomposes at about 2,200° C. It is exceedingly hard, only less so than the diamond.

Silicon carbide is used as an abrasive. Grinding wheels, etc., are made by mixing it with china clay, etc., and firing in a kiln. It is also the best refractory material for the walls of high-temperature furnaces.

**606. Other Silicon Compounds.**—Silicon forms nitrides, sulphides, phosphides, borides, etc., which are not at present of any particular interest.

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## GERMANIUM Ge, 72·60

**607. Germanium and Its Compounds.**—The element germanium is of extreme rarity. The chief mineral from which it is at present extracted is germanite, found in South Africa. This contains up to 6 per cent. of germanium. Some specimens of zinc oxide contain an appreciable quantity of germanium. A good deal of work has recently been done on this element and many of the older data have had to be revised (*v.* table, p. 160).

Germanium is a greyish-white brittle substance of metallic appearance. It melts near a red heat. It is attacked by aqua regia, and nitric acid oxidises it to $GeO_2$. It behaves like a metalloid.

It forms hydrides $GeH_4$, $Ge_2H_6$, $Ge_3H_8$, $(GeH)_x$, $(GeH_2)_x$, which are markedly unstable. It forms two oxides, GeO and $GeO_2$. The former has some basic properties, dissolving in hydrochloric acid to the chloride $GeCl_2$. Germanium dioxide is acidic but shows some trace of basic properties in that it forms the chloride $GeCl_4$ with hydrochloric acid. Germanic acid is extremely weak. A series of chlorine substituted hydrides exists, $GeH_3Cl$, $GeH_2Cl_2$, $GeH_3Br$, $GeH_2Br$, $GeHCl_3$. The existence of these shows the analogy of the element to carbon.

Of the two chlorides, $GeCl_4$ is similar to $SiCl_4$ and $SnCl_4$. Germanous chloride $GeCl_2$ has some resemblance to stannous chloride, and is a powerful reducing agent. Germanium tetrafluoride $GeF_4$ is a colourless fuming gas which, with water, forms fluogermanic acid $H_2GeF_6$. In this germanium resembles silicon. The sulphides are of the metallic type. GeS is formed by the action of hydrogen sulphide on germanous chloride and is known in two forms, orange and black.

## TIN Sn, 118·70

**608. History.**—Tin has been known from very early times. The earliest specimens of bronze—an alloy of copper and tin—are found in Egypt and date from about 2000 B.C. Tin, then, must have been known as early as this. Tin as a separate metal was known to the Greeks and Romans. It was sometimes confused with lead, but was certainly distinguished as a separate metal by the first century A.D. The early alchemists gave to tin the sign of Hermes[1] ☿, while the sign of Zeus[2] 4 was given to *electrum*, a native alloy of gold and silver. In later times (about 700 A.D.) mercury, which had been known for many hundred years, was recognised as a metal and was given the sign of Hermes ☿, while tin took the sign of Zeus, and electrum, now recognised as an alloy, was left without any sign. Tin was used by the Romans for making bronze and solder and also for tinning copper vessels.

**609. Occurrence.**—Tin is widely distributed. It occurs in quantity as the mineral *cassiterite*,[3] tin dioxide $SnO_2$, in the island of Banca, in the Malay States, in Cornwall, Australia, China, Africa,

[1] Lat., Mercurius.
[2] Lat., Jupiter.
[3] Gk. Κασσίτερος, tin.

etc. The Cornish deposits probably supplied the ancient world together with supplies derived from Spain. Herodotus (430 B.C.) and Strabo knew of the Cassiterides or Tin Isles, which have been thought to be the British Isles, but since the description of them does not correspond well with either Cornwall or the Spanish coast, they are quite possibly no more than the early geographers' confused ideas of a district in the far West from which tin was brought.

**610. Manufacture of Tin.**—Tinstone is very dense (sp. gr. *c.* 7). It is occasionally found in alluvial deposits, 'stream tin,' but has usually to be separated from an ore which may contain as little as 0·5 per cent. of tin dioxide. The ore is broken roughly and then crushed by means of stamps weighing 3 cwt. or more, which are mechanically raised and dropped upon the ore, which is contained in a box through which water flows. The water carries off the fine particles of ore. The dense tinstone is deposited sooner than the rocky matter (sp. gr. 2–3). The water flows over a 'buddle'—a simple form of which is an inclined plane with slats fixed at right angles to the flow of the water. The heavy tinstone sinks and is retained by the slats.

The tin ore thus obtained may have to be roasted on a flat furnace bed to remove arsenic and sulphur and is then ready to be smelted. The ore is mixed with a fifth of its weight of carbon in the form of powdered anthracite and heated in a reverberatory furnace. The reaction $SnO_2 + 2C = Sn + 2CO$ takes place and the melted tin sinks to the bottom of the furnace and is tapped off at intervals.

The tin so obtained is far from pure and is further refined by 'poling.' The tin is melted and poles of green wood are thrust into it. Quantities of steam and other gases are evolved from the wood and carry to the surface a scum containing most of the impurity.

Electrolytic methods of refining tin are used, particularly when it contains substantial amounts of other valuable metals, as when obtained from the Bolivian ores. An electrolyte of 8 per cent. sulphuric acid, 3 per cent. benzene-sulphonic acid, and 3 per cent. stannous tin, with a cathode of pure tin and an anode of the impure metal, give on electrolysis a pure metal (99·98 per cent. Sn), while silver, gold, copper, and lead collect in the anode slime.

Tin occurs in three allotropic forms :—

(1) Grey tin, stable below 18° C.

(2) White or tetragonal tin, stable from 18° C. to 161° C.[1]

(3) Rhombic tin, stable from 161° C. to 232° C.

The transformation of grey tin, which is a grey powdery mass, to white tin, the metal as we know it, is reversible and the transition temperature is 18° C.

[1] Several discrepant values are given.

18° C.
Grey tin ⇌ White tin.

Accordingly, on an ordinary English winter day, white tin should be converted into a grey powdery solid. This, of course, does not happen, and it is only in excessively cold winters, such as are experienced in Russia, that this change occurs. It is a good example of suspended transformation, analogous to the super-cooling of a liquid. If the white tin, at any temperature below 18° C., is brought into contact with a little grey tin, the change then proceeds. This phenomenon gave rise to the name 'tin-pest', sometimes applied to the change. The starting of the change by contact with grey tin is analogous to the addition of a crystal of solid to a super-cooled liquid.

The change is very slow, because both phases are non-volatile solids.

**611. Properties of Tin.**—White tin is a silver-white metal. It is fairly hard and is notably crystalline in structure. A rod of tin, when bent, makes a perceptible creaking sound, the 'cry of tin,' which is probably caused by the crystals rubbing against each other. Tin melts at 232° C., a melting point lower than that of any common metal and is therefore employed in alloys of low-melting point. Tin is very malleable and ductile at about 100° C. and is then easily rolled into tinfoil or 'silver paper.' Thin sheets of tin made in this way are used for wrapping purposes and for the manufacture of collapsible tubes for toothpaste, etc. Tin is, for a metal, a moderately good conductor of electricity.

Tin is not oxidised at the ordinary temperature, but melted tin slowly forms a scum of white tin dioxide,

$$Sn + O_2 = SnO_2.$$

Tin is readily attacked by chlorine, yielding the liquid stannic chloride (*q.v.*),

$$Sn + 2Cl_2 = SnCl_4.$$

It reacts with sulphur, forming stannic sulphide (*q.v.*).

Tin is not attacked by water or steam, but is readily attacked by mineral acids. With hydrochloric acid, stannous chloride (*q.v.*) is produced,

$$Sn + 2HCl = SnCl_2 + H_2.$$

Concentrated sulphuric acid oxidises it to tin dioxide, which probably forms the unstable stannic sulphate,

$$Sn + 4H_2SO_4 = Sn(SO_4)_2 + 4H_2O + 2SO_2.$$

The reaction of nitric acid with tin is complex. Dilute nitric acid yields stannous nitrate, while stronger and concentrated acid yields $\beta$-stannic acid $H_2Sn_5O_{11}.4H_2O$ or $(SnO_2.H_2O)_5$. The chief gas evolved is nitrous oxide $N_2O$. Ammonia and nitrogen are formed in small proportion and with dilute acids some nitric oxide NO. Perhaps the most representative of the several equations to be written is

$$2Sn + 2HNO_3 + aq. = 2SnO_2\,aq. + N_2O + H_2O,$$

but, of course, several other simultaneous reactions occur.

Weak acids attack tin only slightly, and hence tin-plated iron cans (' tins ') can be used for preserving acid fruits.

Alkalis attack tin readily. If tin is heated with caustic soda *sodium stannite* is formed (cf. action of zinc and aluminium),

$$Sn + 2NaOH = Na_2SnO_2 + H_2.$$

**612. Uses of Tin.**—Tin is used in enormous quantities for making 'tin plates.' Thin rolled sheets of mild steel are freed from oxide by 'pickling' them with warm dilute sulphuric acid. They are washed and dried, annealed and again pickled. They are passed mechanically into a bath of melted tin, on which floats a flux of melted zinc chloride (the function of which is to cause the tin to adhere), then out through a part of the bath which is coated with molten grease. A pair of rollers squeezes off any surplus metal. Other uses of tin are in the manufacture of bronze (§ 279), solder, type metal, and bearing metal.

**613. Atomic Weight of Tin.**—Dulong and Petit's rule, the vapour density of its volatile compounds and the periodic rule indicate an atomic weight of about 120 for tin. Its equivalent being nearly 59 in stannous and 30 in stannic compounds, its valencies are 2 and 4.

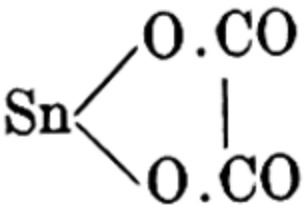
The atomic weight of tin has been best determined by converting stannic chloride $SnCl_4$ into tin by electrolysis. From this and other methods a value of 118·70 has been obtained. Both tin and germanium have a large number of isotopes. No less than eleven isotopes of tin with atomic weights between 112 and 124 have been detected.

**614. Tin Hydride $SnH_4$.**—Tin forms a very unstable gaseous hydride, $SnH_4$. Traces are formed when tin is dissolved in dilute acid (4N), or when stannous sulphate is electrolysed, or when hydrochloric acid acts upon an alloy of tin and magnesium. It has been isolated by condensing it with liquid air and purified by fractionating the liquefied gas. The gas decomposes spontaneously to tin and hydrogen at room temperature.

**615. Tin Oxides.**—There are two oxides of tin :—

| | |
|---|---|
| Stannous oxide . . . . | $SnO$ |
| Stannic oxide . . . . . | $SnO_2$ |

**616. Stannous Oxide SnO** is made by heating stannous oxalate,



$$= SnO + CO + CO_2,$$

or by the action of alkalis on stannous chloride solution and careful heating of the precipitated stannous hydroxide in absence of air,

$$2NaOH + SnCl_2 = Sn(OH)_2 + 2NaCl$$
$$Sn(OH)_2 = H_2O + SnO.$$

Its colour varies from brown or dark grey to black. Stannous oxide burns in air with incandescence, forming stannic oxide,

$$2SnO + O_2 = 2SnO_2.$$

It has otherwise the usual properties of an amphoteric metallic oxide, forming salts with acids.

It dissolves in alkalis giving the so-called stannites, which are probably colloidal solutions of the oxide.

**617. Stannic Oxide $SnO_2$** occurs native as *cassiterite* or *tin stone*. It is prepared by heating tin in air, or by heating the metastannic acid obtained when nitric acid acts on tin.

$$H_2Sn_5O_{11} . 4H_2O = 5SnO_2 + 5H_2O.$$

Tin dioxide is a white powder. It is unattacked by any acids except concentrated sulphuric acid, in which it dissolves. The solution decomposes on dilution, giving the oxide once more, and may contain the unstable stannic sulphate $Sn(SO_4)_2$ (*q.v.*). It is attacked by alkalis, forming sodium stannate,

$$SnO_2 + 2NaOH = Na_2SnO_3 + H_2O.$$

Stannic oxide is known in commerce as putty powder, and is used as a polishing medium. It imparts an intense whiteness to glass, and is used to make the white glazes for tiles, milk-glass shades, etc.

**618. Stannic Acids.**—The stannic acids, like the silicic acids, are of somewhat indefinite composition. They may be regarded as hydrated stannic oxide, and have a composition varying from $SnO_2 . H_2O$ or $H_2SnO_3$ to $SnO_2 . 2H_2O$ or $Sn(OH)_4$.

They are probably highly polymerised. There are two modifications α-stannic acid and β-stannic acid. They differ in the ease with which they are attacked by acids, etc., but the difference between them is perhaps only a difference of size of particles.

*α-stannic acid* is made by the action of ammonia on stannic chloride.

$$4NH_4OH + SnCl_4 = 4NH_4Cl + Sn(OH)_4,$$

or by the action of acids upon a stannate,

$$Na_2SnO_3 + 2HCl = 2NaCl + SnO(OH)_2.$$

Note that the formulæ of the acids produced by the two methods appear different. There is not, however, any apparent difference in the product.

The composition of stannic acid varies with the amount it has been dried. At a red heat it forms tin dioxide,

$$Sn(OH)_4 = SnO_2 + 2H_2O.$$

Stannic acid is a gelatinous whitish substance or, if further dried, an amorphous powder. It is a colloid like silicic acid and may, like the latter, be prepared in a soluble form.

Stannic acid forms a large series of salts; the sodium salt is of technical importance and is discussed below. Colloidal stannic acid is of interest for its formation of *purple of Cassius* (*v.* under Gold, § 327).

*β-stannic acid* is obtained by the action of tin on concentrated nitric acid. It differs from α-stannic acid in that it is not readily dissolved by acids. It is of somewhat indefinite composition but appears to be $H_2Sn_5O_{11}.4H_2O$ or $[SnO_2.H_2O]_5$, since its sodium salt and potassium salts have formulæ $M_2Sn_5O_{11}.4H_2O$.

**619. Sodium Stannate $Na_2SnO_3 . 3H_2O$** is an article of commerce, being used as a mordant in dyeing (*v.* § 484). It is made by fusing tin with caustic soda, sodium nitrate and salt. The sodium nitrate oxidises the tin to the dioxide and this reacts with the caustic soda,

$$SnO_2 + 2NaOH = Na_2SnO_3 + H_2O.$$

It is a white crystalline salt, very soluble in water. It crystallises with 3 molecules of water, which cannot be removed by drying. The salt may therefore be $Na_2[Sn(OH)_6]$.

## Salts of Tin

Tin forms two series of salts, the stannous, in which the metal is divalent, and the stannic, in which its valency is four.

**620. Oxysalts of Tin.**—Both stannous sulphate ($SnSO_4$) and stannic sulphate $Sn(SO_4)_2$, exist and are made by dissolving the respective hydroxides in sulphuric acid. Stannic sulphate is hydrolysed by water.

*Stannous nitrate* $Sn(NO_3)_2$ is obtained by dissolving tin in very dilute nitric acid. *Stannic nitrate* $Sn(NO_3)_4$ can be made by dissolving stannic hydroxide in nitric acid.

There is no carbonate of tin.

**621. Sulphides of Tin.**—The sulphides of tin are of some interest as occurring in qualitative analysis. Brown stannous sulphide is precipitated when hydrogen sulphide is passed through a solution of a stannous compound,

$$Sn^{++} + S^{--} = SnS.$$

A stannic compound gives a dirty yellow precipitate of stannic sulphide,

$$Sn^{++++} + 2S^{--} = SnS_2.$$

These substances are both soluble in *yellow* ammonium sulphide (containing excess of sulphur) to form ammonium thiostannate,

$$SnS + S + (NH_4)_2S = (NH_4)_2SnS_3$$
$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3.$$

This property they share with the sulphides of arsenic and antimony (*q.v.*). Stannic sulphide is sometimes used as a bronzing powder, 'Mosaic gold.' For this purpose mixtures of tin, sulphur and ammonium chloride are sublimed.

**622. Stannous chloride** is the most important stannous salt. It is readily prepared by the action of tin on hydrochloric acid,

$$Sn + 2HCl = SnCl_2 + H_2.$$

Stannous chloride is a white salt, which crystallises in monoclinic prisms of composition $SnCl_2.2H_2O$. It is soluble in water but reacts with it,

$$SnCl_2 + H_2O \rightleftharpoons Sn(OH)Cl + HCl,$$

precipitating basic tin chloride. The addition of HCl causes the precipitate to re-dissolve, as the above equilibrium equation would lead us to expect.

Stannous chloride when heated gives off water, melts at 249° and boils at about 606° C.

With alkalis, white stannous hydroxide is formed,

$$Sn^{++} + 2OH^- = Sn(OH)_2 \downarrow .$$

which re-dissolves in excess of alkali, forming a stannite. Hydrogen sulphide precipitates brown stannous sulphide from solutions of stannous chloride,

$$Sn^{++} + S^{--} = SnS \downarrow .$$

It has the usual properties associated with a chloride.

Stannous chloride is one of the most useful reducing agents. All the stannous salts are readily oxidised to stannic compounds.

Among these reactions we may note the reduction of ferric salts to ferrous salts,

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4,$$

or

$$2Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++},$$

the reduction of mercuric salts to mercurous salts, and finally mercury. Thus, if solutions of stannous chloride and mercuric chloride are mixed, white mercurous chloride is precipitated and slowly becomes blackened by the separation of mercury,

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2 \downarrow$$
$$SnCl_2 + HgCl_2 = SnCl_4 + Hg.$$

It also reduces cupric salts to cuprous salts. It reduces nitric acid to hydroxylamine (§ 705) and is a useful reducing agent in organic chemistry. Thus, by shaking nitronaphthalene with a solution of stannous chloride in hydrochloric acid we obtain naphthylamine,

$$C_{10}H_7.NO_2 + 6HCl + 3SnCl_2 = C_{10}H_7NH_2 + 2H_2O + 3SnCl_4.$$

Stannous chloride is used also as a mordant in dyeing.

*Stannic chloride* was first prepared by the Dutch chemist, Libavius, in 1605, and was for long known as *fuming liquor of Libavius*. It is now prepared by the action of chlorine upon tin by the method described under phosphorus trichloride (Fig. 150). The tin is placed in the retort and heated in a current of chlorine,

$$Sn + 2Cl_2 = SnCl_4.$$

The liquid stannic chloride is condensed.

Stannic chloride resembles the chloride of a non-metal in its physical properties. It is a colourless mobile liquid of sharp, unpleasant odour. It emits dense white fumes when exposed to moist air. Stannic chloride boils at 114° C.

The action of moisture converts it into a solid hydrate, $SnCl_4.5H_2O$, and the reaction with much water forms a clear solution from which basic chlorides and finally α-stannic acid are precipitated,

$$SnCl_4 + H_2O \rightleftharpoons SnCl_3(OH) + HCl$$
$$SnCl_3OH + 3H_2O \rightleftharpoons Sn(OH)_4 + 3HCl.$$

It thus resembles such covalent chlorides as those of aluminium, arsenic and antimony rather than those of the heavy metals, which are ionic compounds and true salts.

Stannic chloride forms double salts, such as $SnCl_4.2NH_4Cl$ ('pink salt'). This is ammonium stannichloride $(NH_4)_2SnCl_6$, analogous to potassium fluosilicate $K_2SiF_6$. The salt is used as a mordant in dyeing. The acid $H_2SnCl_6.6H_2O$ is known.

The *bromides* of tin much resemble the chlorides.

**623. Detection of Tin.**—Tin is detected by the precipitation of its sulphides from an acid solution. The sulphides are distinguished from those of mercury, copper, lead, bismuth and cadmium by their solubility in ammonium sulphide. It may be detected in presence of arsenic and antimony sulphides by converting all three sulphides into the higher chlorides, and then precipitating stannic hydroxide with ammonia. Antimony and arsenic under these conditions form the soluble arsenate and antimonate and give no precipitate.

**624. Estimation of Tin.**—Tin is estimated in various ways. Stannous salts are readily titrated with iodine according to the reaction

$$Sn^{++} + 2I = Sn^{++++} + 2I^-.$$

Stannic salts may be reduced by heating them in acid solution with sheet nickel,

$$Sn^{++++} + Ni = Sn^{++} + Ni^{++},$$

and then titrated iodimetrically as above.

Tin may be estimated gravimetrically in its alloys by oxidising the metal to β-stannic acid with nitric acid, other metals forming soluble nitrates or oxyacids. This is filtered off, ignited and weighed as tin dioxide. Its salts may be oxidised, if need be, to the stannic condition, precipitated as stannic hydroxide, which is ignited and weighed as the dioxide.

## LEAD Pb, 207·21

**625. History.**—The metal lead has been known from very remote times. The Egyptians were acquainted with it at a very early date. The Romans worked lead extensively and made lead pipes up to 9 inches diameter. Lead was associated with the planet Saturn, perhaps because the heaviness and softness of lead suggested the slowest moving planet and also, perhaps, because the colour of the metal suggested the peculiar light of that planet. The sign ♄ represents both lead and Saturn.

**626. Occurrence.**—Lead ores are of wide distribution. Lead is found in almost every part of the world. Most of the world's lead comes from the U.S.A., Canada, Australia and Burma. Very little is mined in the United Kingdom. The most important ores are *galena*, lead sulphide; *cerussite*, lead carbonate; and *anglesite*, lead sulphate.

**627. Manufacture.**—Lead is obtained from galena by—

(1) Sintering;

(2) Smelting in a blast furnace.

Numerous processes are employed in different parts of the world, but the modern method, giving most of the lead produced to-day, operates as follows :—

(1) Crushed ore, together with a little coke and limestone flux, is carried continuously through a sintering machine on a moving band, where it is ignited and subjected to a down-draught of air (Fig. 123). Here the following reactions take place :—

(i) $C + O_2 \rightarrow CO_2$

(ii) $2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$

(iii) $2SO_2 + O_2 \rightarrow 2SO_3$

(iv) $PbO + SO_3 \rightarrow PbSO_4$

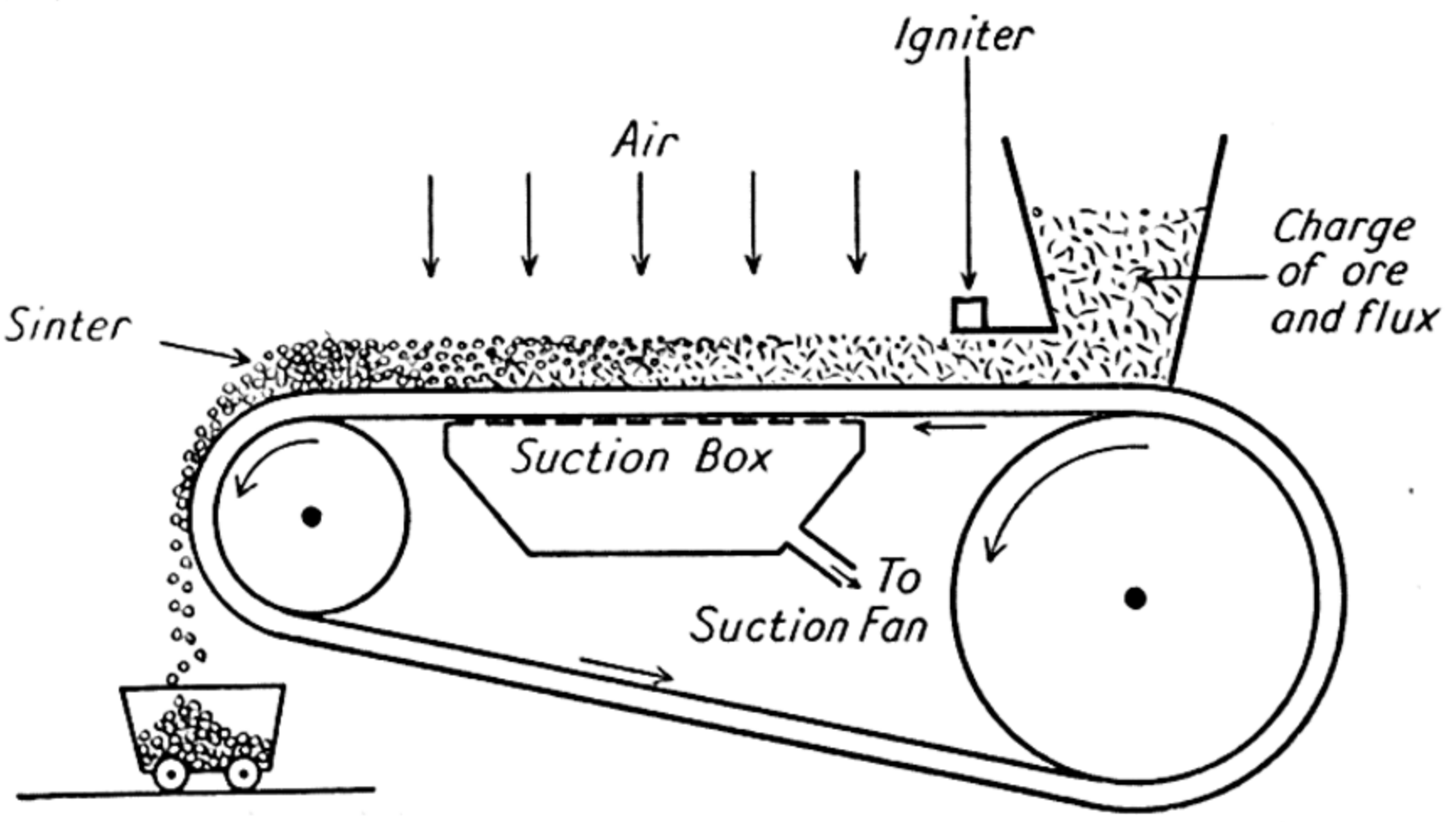



FIG. 123.—Sintering plant for oxidation of lead-ore.

Reactions (i), (ii) and (iii) are strongly exothermic and thus the temperature is maintained throughout the operation. Sinter is continuously removed at the end of the moving iron track, and transferred to the blast furnace. Galena itself is friable, brittle, and fuses easily, and thus cannot be used directly in the blast furnace, but the sintering process provides a hard, strong, porous clinker, suitable for this purpose and consisting of the oxide, sulphide and sulphate of lead together with earthy impurities.

(2) The sinter, with limestone, coke and a little iron ore is smelted in a small blast furnace (Fig. 132A). The main reactions occurring are :—

$$PbO + CO \rightarrow Pb + CO_2$$
$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2$$
$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$
$$FeO + PbS + C \rightarrow Pb + FeS + CO$$

The silica, which is always contained in the lead ore, forms ferrous and calcium silicates. The fused mass separates into three mutually insoluble layers, the uppermost being a *slag* of silicates, the middle one a *matte* of ferrous and sometimes copper sulphides, and the lowest molten lead. These are tapped off separately. Low grade silver and gold ore is often added to the charge and these precious metals are separated at a later stage from the lead.

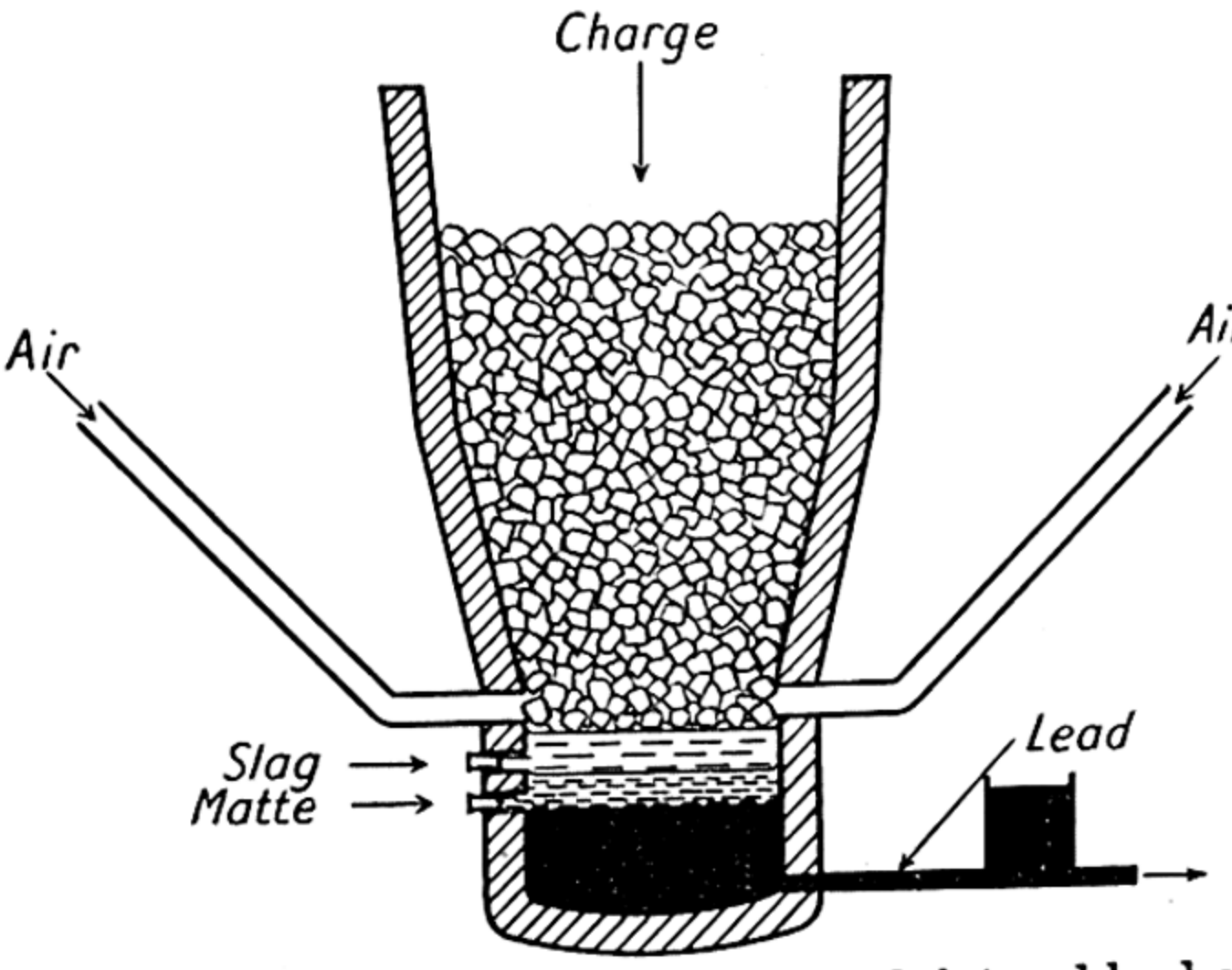



FIG. 123A.—Blast-furnace for smelting of sintered lead-ore.

The lead often contains antimony, zinc, etc., which make it hard. It is usually purified by being melted and exposed to a current of hot air. The other metals, except the noble metals, are preferentially oxidised and raked off as a scum of oxides. The lead is then desilverised (§ 300)—for silver is always contained in lead ore—and then is fit for most general purposes. In the manufacture of white

lead however (§ 640), traces of silver and bismuth impart a noticeable tinge to the pigment, and so a certain amount of lead is refined electrolytically for this purpose. An electrolyte of lead fluosilicate together with some free fluosilicic acid is used with a cathode of pure electrolytic lead and anodes of the crude metal. A lead of a high degree of purity is produced and precious metals are recovered from the anode slime.

**628. Properties of Lead.**—Lead is a blue-grey metal. Its lustre is only seen on a newly-cut surface. The clean metal oxidises very quickly, but the action ceases as soon as it is coated with a film of oxide. It emits a peculiar odour when rubbed between the fingers. Lead may readily be obtained in a crystalline state by precipitation. If a zinc rod be hung in a weak solution of lead acetate, the 'lead tree,' a mass of arborescent crystals, is produced as a result of the reaction,

$$Zn + Pb^{++} = Zn^{++} + Pb.$$

Lead is very soft. It can be scratched with the finger nail and it leaves a mark upon white paper. It is made harder by traces of impurities, in particular, antimony.

Lead is very dense, the sp. gr. being 11·34–11·37 at 4° C. It has a high coefficient of expansion, 0·000037, and very low specific heat, 0·0303 at 0° C. Lead melts at 325° C. and boils at about 1,150° C.

Lead is not oxidised in the compact state except in so far as to form a superficial coating, thought to be a lower oxide. When melted in air it is oxidised and is gradually converted into lead monoxide, *litharge*,

$$2Pb + O_2 = 2PbO.$$

Chlorine and sulphur both attack lead when heated, forming the chloride $PbCl_2$, and sulphide PbS, respectively.

Lead is slightly attacked by water containing air in solution, the hydroxide and carbonate being formed. This is a serious menace where much lead piping is used for water supplies, for lead is a cumulative poison, and minute amounts taken daily may prove dangerous. Hard water does not affect lead, for a layer of lead carbonate formed on the surface arrests the action. Moorland water containing traces of free organic acids is the most dangerous.

Lead is not appreciably attacked by acids other than nitric acid, hot hydrochloric acid, and hot concentrated sulphuric acid. It is therefore a useful material for industrial purposes where acid-proof tanks, etc., are required. Boiling hydrochloric acid forms lead chloride,

$$Pb + 2HCl = PbCl_2 + H_2,$$

and nitric acid the nitrate, nitric oxide and nitrogen peroxide being formed as the chief gaseous products,

$$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O.$$

Concentrated nitric acid has not much action on lead, for lead nitrate is insoluble in the concentrated acid and forms a protective coating.

Concentrated sulphuric acid, if hot and over 60 per cent. strength, attacks lead, though the action is somewhat retarded by the coating of insoluble sulphate produced,

$$Pb + 2H_2SO_4 = PbSO_4 + 2H_2O + SO_2.$$

**629. Uses of Lead.**—Lead finds its chief uses in the manufacture of sheet lead for roofing, lead piping, shot, solder, etc. Its resistance to corrosion renders it useful in constructing chemical plant of various kinds, sulphuric acid chambers, etc.

**630. Atomic Weight of Lead.**—The exact atomic weight of lead is of particular interest because of its variation with the source from which the lead is derived. The end product of the decomposition of the three series of radio-elements (p. 817) is in each case lead, but calculation shows that the lead derived from uranium should have an atomic weight of about 206, while that from thorium should have atomic weight 208·4. The examination of lead from different sources indicates that these values are correct, for the atomic weight of lead derived from uranium minerals appears to be nearly 206·0–206·1, that of ' ordinary ' lead is about 207·2, while that of lead from thorium minerals has been given values as high as 207·9 and 208·4. The equivalent of lead is 103·61 in its normal salts. Dulong and Petit's law indicates a value of about 200. Its analogy to tin and consequent position in the Periodic table confirm this value, as do the vapour densities of some organic lead compounds, such as lead tetra-ethyl $Pb(C_2H_5)_4$.

The exact atomic weight has usually been determined by finding the weight of silver chloride precipitated from silver nitrate solution by highly purified lead chloride.

The atomic weight of ordinary lead from non-radioactive sources has a constant value, which is best taken as 207·22.

Three isotopes of lead, of atomic weights 206, 207, 208, are known to exist.

## Compounds of Lead

**631. Lead Hydride.**—A volatile lead hydride, analogous to tin hydride, has been reported and probably has the formula $PbH_4$.

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**632. Oxides of Lead.**—There are five oxides of lead—

| | | |
|---|---|---|
| Lead suboxide . . | $Pb_2O$ | |
| Lead monoxide . . | PbO | Litharge. |
| Triplumbic tetroxide . | $Pb_3O_4$ | Red lead. |
| Lead sesquioxide . . | $Pb_2O_3$ | |
| Lead dioxide . . | $PbO_2$ | |

*Stability of Oxides.*—As a rule, where an element has several oxides, each of these at temperature above, say, 200° C. to 300° C., exerts a measurable dissociation pressure of oxygen in consequence of a reaction such as

$$2M_2O_3 \rightleftharpoons 4MO + O_2.$$

If this dissociation pressure is less than the partial pressure of oxygen in the surrounding atmosphere (0·2 atm. in air) oxygen will combine with MO and form $M_2O_3$. If it is greater, then $M_2O_3$ will decompose giving MO. The dissociation pressure always increases as the temperature rises.

With the lead oxides, it follows from the above that in air and *at equilibrium* only one oxide will be permanently stable at any one temperature.

Thus, lead monoxide, PbO, is stable in air above 550° C.; lead sesquioxide, $Pb_2O_3$, is stable in air from 450° C. to 550° C.; red lead, $Pb_3O_4$, is stable in air from 350° C. to 450° C. Accordingly, any of these oxides can be made by heating any oxide of lead to the above temperatures in air till reaction ceases—often a slow process.

Lead dioxide is not in equilibrium with oxygen at any temperature; it is unstable and exists permanently at room temperature only because its rate of decomposition is so slow as to be inappreciable.

In the same way, lead monoxide is permanent in air at room temperature because its reaction with oxygen is then almost infinitely slow.

**633. Lead Suboxide** is of small importance. It is made by heating lead oxalate out of contact with air,

$$2Pb(C_2O_4) = Pb_2O + CO + 3CO_2.$$

**634. Lead Monoxide, Litharge, Massicot, PbO.**—Litharge and massicot are chemically the same, but the former has been made at a temperature high enough to fuse it, while the latter is prepared at a moderate temperature only.

In the laboratory lead oxide may be made by heating the carbonate, nitrate or hydroxide.

On the commercial scale it is made by heating lead to a high temperature and continually skimming off the melted litharge as it is produced,

$$2Pb + O_2 = 2PbO.$$

The litharge then only requires to be ground.

Litharge is a pale yellow to reddish yellow solid of high density (sp. gr. about 9·1). The colour varies a good deal, and it is clear that there exist a yellow form and a reddish form. When heated to redness it fuses to a clear yellow liquid. Litharge is easily reduced to lead when heated in a current of hydrogen,

$$PbO + H_2 = Pb + H_2O.$$

Litharge has the usual reactions of a basic oxide, forming salts with acids, etc. It also reacts with alkalis, forming *plumbites*,

$$2NaOH + PbO = Na_2PbO_2 + H_2O.$$

It finds uses in glass making (*v.* § 600), and in the manufacture of lead salts.

**635. Triplumbic Tetroxide, Red Lead, Minium, $Pb_3O_4$.**—Red Lead was known to the ancients as a pigment. It is prepared by converting lead at a low temperature into *massicot*, unfused lead oxide, and then after grinding this finely, heating the lead oxide to a carefully regulated temperature in special ovens. The process is slow, occupying some hours,

$$6PbO + O_2 = 2Pb_3O_4.$$

Red lead is a brilliant red crystalline powder. When heated it changes colour, becoming almost black; the colour, however, returns on cooling (cf. mercuric oxide). Further heating converts it into the monoxide,

$$2Pb_3O_4 = 6PbO + O_2.$$

Nitric acid converts it into lead nitrate and lead peroxide,

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

In this and other respects it behaves as if it were a compound of lead monoxide and dioxide, perhaps lead plumbate $Pb_2.PbO_4$.

Hydrochloric acid forms lead chloride and chlorine is evolved,

$$Pb_3O_4 + 8HCl = 3PbCl_2 + 4H_2O + Cl_2.$$

Red lead finds numerous uses. In oil paints it is at once a fine red pigment and a 'drier.' As a pigment it is not very permanent. Vermilion is much superior but far more expensive. Red lead, mixed with oil, is used as a cement for jointing pipes, etc. It is also used in glass manufacture.

**636. Lead Sesquioxide, $Pb_2O_3$,** is a yellowish-red powder, similar in behaviour to red lead.

**637. Lead Dioxide, Lead Peroxide, $PbO_2$.**—Lead dioxide, often incorrectly called lead peroxide, is made—

(1) by the action of nitric acid on red lead ;

(2) by the action of an alkaline oxidising agent, such as bleaching powder on a lead salt.

(1) The first method gives a poor yield, but presents no difficulties :

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

The lead dioxide is filtered off, washed and dried.

(2) The process is conveniently carried out as follows : A solution of lead acetate in water is mixed with an excess of a suspension of bleaching powder and heated on the water-bath. The supernatant liquid is decanted from the heavy brown precipitate,

$$Pb(C_2H_3O_2)_2 + Ca(OH)_2 = Pb(OH)_2 + Ca(C_2H_3O_2)_2$$
$$Pb(OH)_2 + CaOCl_2 = PbO_2 + H_2O + CaCl_2,$$

which is then well stirred with hot dilute nitric acid in order to remove any bleaching powder. It is then filtered off, well washed and dried.

Lead dioxide is a dark reddish-brown powder. The commercial material usually contains lower oxides which may be removed by extraction with warm dilute nitric acid. When heated, it is readily decomposed into lead monoxide and oxygen.

It is a powerful oxidising agent. Many inflammable substances burn violently or explode when heated or ground with it.

Lead dioxide is not affected by most acids. When dropped into ice-cold concentrated hydrochloric acid it gives a bright yellow liquid which contains hexachloroplumbic acid (§ 649a)

$$PbO_2 + 4HCl \rightleftharpoons PbCl_4 + 2H_2O$$
$$2HCl + PbCl_4 \rightleftharpoons H_2PbCl_6$$

On heating the liquid lead chloride is precipitated and chlorine is evolved

$$H_2PbCl_6 = PbCl_2 + 2HCl + Cl_2.$$

The reaction between hot hydrochloric acid and lead dioxide may be summarised in the equation

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$$

With alkalis lead dioxide forms plumbates, analogous to the stannates.

Lead peroxide finds an important application in the *accumulator*.

The accumulator consists in its simplest form of two perforated lead plates,

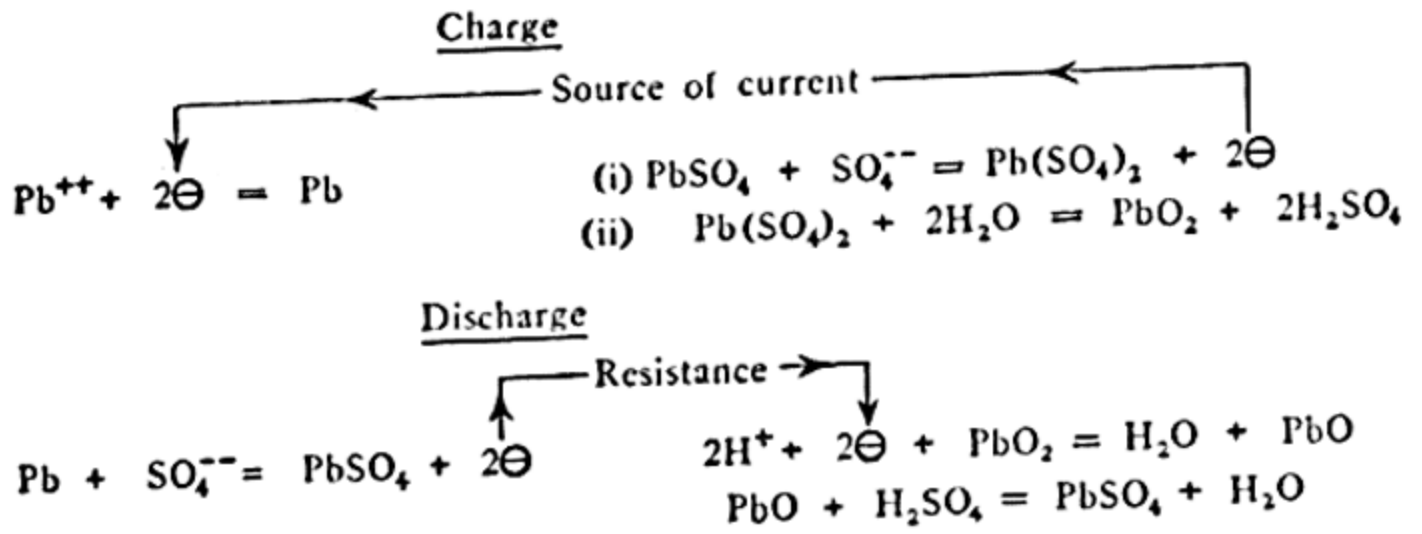
the perforations in which are filled with a paste of lead oxide. When these are immersed in dilute sulphuric acid the lead oxide is converted into lead sulphate. When a current is passed through a cell consisting of two such plates immersed in dilute sulphuric acid the latter is not electrolysed, for the over-voltage is such that the lead sulphate is electrolysed instead. Lead is produced at the cathode and the sulphate group liberated at the anode oxidises the lead to the disulphate which decomposes, giving the peroxide,

$$PbSO_4 + SO_4 = Pb(SO_4)_2$$
$$Pb(SO_4)_2 + 2H_2O = PbO_2 + 2H_2SO_4.$$

When all the lead sulphate has gone the dilute sulphuric acid is next electrolysed and 'gassing' commences.

The accumulator has now one plate of lead and one of lead peroxide and is said to be charged. It shows an E.M.F. of about 2 volts.

At the lead plate lead combines with sulphate ion, forming lead sulphate and liberating electrons, while at the lead peroxide electrode the hydrion of the acid, $H^+$, combines with the electrons of the current, forming hydrogen, which reduces the lead peroxide to lead oxide, and this reacts with the acid, forming lead sulphate. The accumulator thus becomes *discharged* and the coating on its plates reconverted into lead sulphate.




The E.M.F. of the cell remains remarkably constant during discharge. This is due to the small solubility of lead sulphate, which keeps the concentration of lead ion small and nearly constant.

**638. Lead Hydroxide $Pb(OH)_2$** is a white solid, prepared by the action of an alkali on a soluble lead salt.

When heated it yields lead monoxide. It dissolves in acids, forming lead salts, and in alkalis, forming plumbites, *e.g.*, $K_2PbO_2$.

**639. General Properties of Lead Salts.**—Lead salts are in general colourless. They are poisonous (§ 641). In solution they furnish the lead ion, $Pb^{++}$. Solutions containing this ion give several characteristic reactions. Lead is precipitated from these solutions by zinc and other electropositive metals. Many lead salts are insoluble in water and many characteristic precipitates are therefore produced from lead salts.

With chlorides white lead chloride $PbCl_2$, soluble in hot water, is precipitated.

The yellow chromate $PbCrO_4$ and the yellow iodide $PbI_2$ are obtained when solutions of lead salts are mixed with solutions of chromates (not too acid) or iodides, respectively.

With alkalis, white lead hydroxide, soluble in excess of alkali, is precipitated. Hydrogen sulphide precipitates black lead sulphide PbS. Sulphuric acid or sulphates precipitate the white lead sulphate $PbSO_4$.

**640. Lead Carbonate, White Lead, $2PbCO_3 . Pb(OH)_2$.**—Normal lead carbonate $PbCO_3$ is a common mineral known as *cerussite*. Lead carbonate, as prepared by precipitation or by the commercial methods described below, is always a basic salt.

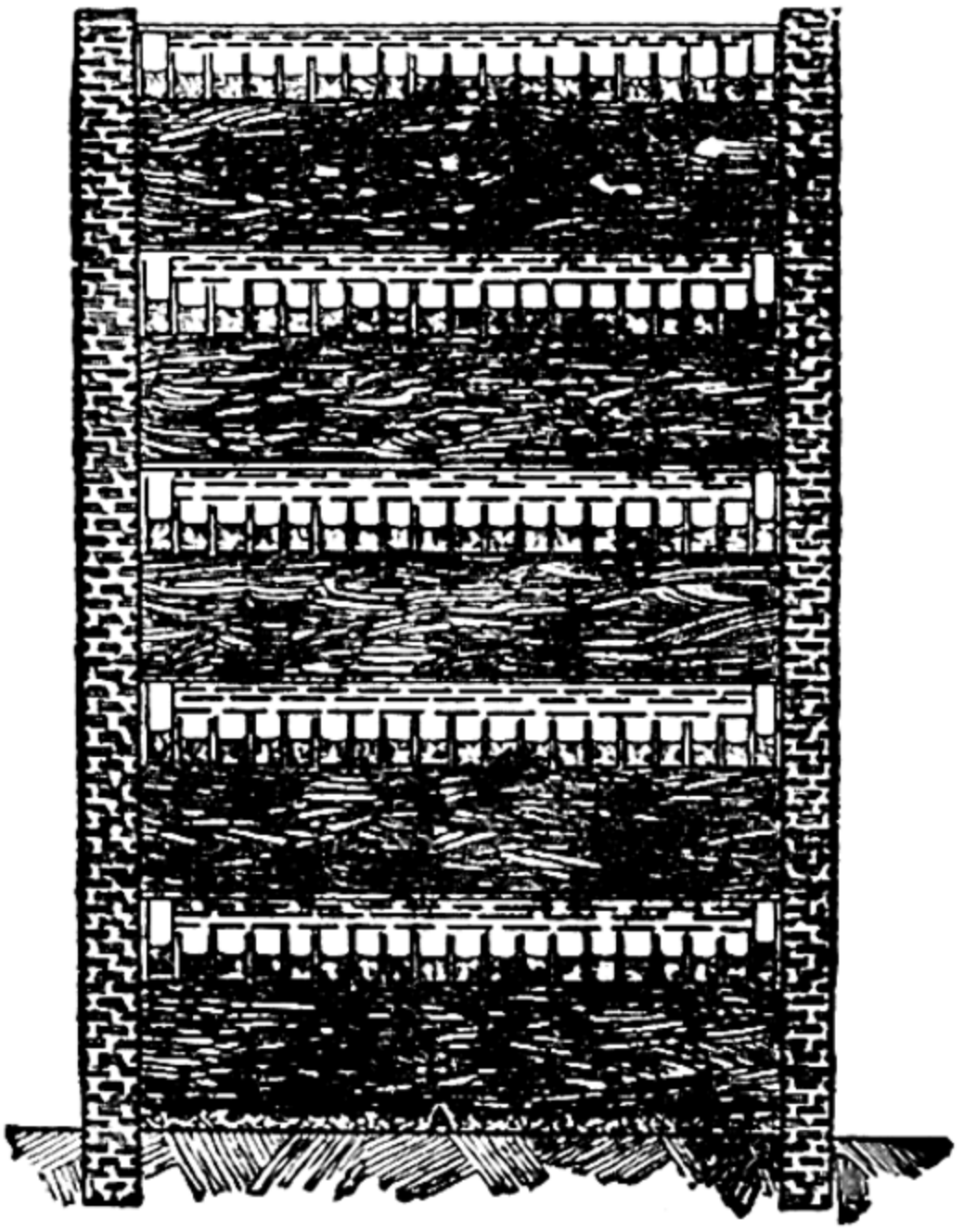


FIG. 124.—Manufacture of white lead by Stack process.

The commercial lead carbonate—white lead—is made by a peculiar process. While there are numerous much simpler chemical methods of making lead carbonate, it cannot by any of them be produced in the same state of fine subdivision and opacity which gives to whitelead its great *covering power* and consequent value as a pigment.

The stack process, as it is called, is carried out as follows : Lead is cast into sheets perforated like gratings and also into small 'stars' or 'buckles.'

In brickwork chambers, say about 15 feet square and 25 feet high, there is built up a 'stack' composed as follows : First a layer of

ashes (A), then a layer (B) of spent tan bark (the moist residue of oak bark, etc., from which tannin has been extracted). This tan bark ferments, and in so doing becomes hot and gives off carbon dioxide. On a bed of this tan, 3 feet deep, are set pots partly filled with dilute acetic acid (2–3 per cent.) and containing some of the small leaden 'stars' or 'buckles.' On top of the pots are laid the gratings of metallic lead, forming a layer about 5 inches deep, and above these wooden boards supported on the taller pots which stand round the outside of the stack. On top of all this is built up another bed of tan, pots, lead, etc., and these beds are repeated up to the top of the stack. The temperature is carefully regulated by ventilation and the stack is left for three months.

The tan ferments, becoming hot and producing carbon dioxide and moisture. The heat volatilises some acetic acid. The heat and moisture probably first cause the lead to form the hydroxide, and the acetic acid then causes the formation of basic lead acetate, which is again decomposed by the carbon dioxide produced by the fermentation, so forming white lead and acetic acid, which once again attacks the lead.

The chemical reactions may be :

$$(1) \qquad 2Pb + 2H_2O + O_2 = 2Pb(OH)_2.$$

$$(2) \qquad Pb(OH)_2 + 2C_2H_4O_2 = Pb(C_2H_3O_2)_2 + 2H_2O.$$

$$(3) \qquad 2Pb(C_2H_3O_2)_2 + Pb(OH)_2 = Pb(OH)_2.[Pb(C_2H_3O_2)_2]_2.$$

$$(4) \qquad Pb(OH)_2.[Pb(C_2H_3O_2)_2]_2 + 2CO_2 + 2H_2O = Pb(OH)_2.[PbCO_3]_2 + 4C_2H_4O_2$$

The stack is finally taken down and the white lead is separated from the unchanged metal and finely ground.

The stack process takes some 100 days to reach completion, and so modifications have been introduced to speed up the reactions. In the Carter process molten lead is atomised in an air blast, and the finely divided metal so produced is treated in a revolving wooden drum with a spray of acetic acid, carbon dioxide from coke, and air. After about 8 days the conversion into white lead is complete, and the product is finer and more uniform than that produced by the stack process, though the reactions are the same.

White lead is also produced electrolytically. The cell consists of lead anodes immersed in the anolyte of sodium acetate, separated from the catholyte of sodium carbonate and the iron cathodes by a fabric diaphragm. When current flows, lead dissolves as lead acetate but, on meeting carbonate and hydroxide ions migrating to the anode from the cathode compartment, is almost immediately precipitated as white lead. The anolyte is continuously circulated so that the white lead is carried out of the cell to be settled, filtered, washed and finally dried.

White lead has the ordinary chemical properties of a basic carbonate (cf. § 567). It is remarkable for its singular covering power, which makes it by far the best white pigment. Its disadvantages are, first, its ready discoloration by hydrogen sulphide—always present in town air—in consequence of the formation of brown-black lead sulphide and, secondly, its poisonous character.

**641. Lead Poisoning.**—Lead compounds are all poisonous. They are cumulative poisons, producing in those who take small quantities of lead for long periods, first colic, then fits, paralysis and ultimately death. It has been stated that it is impossible to poison a man with a single dose of a lead salt, however large; the author does not recommend the student to take the risk.

Lead compounds are therefore dangerous to those who work with them habitually. The worker with lead only suffers if he actually takes it into his system, and accordingly those who inhale lead-containing dust, such as painters and employees in white lead works, are the chief sufferers. If thorough cleanliness is observed and dust is kept down, the poisoning is avoidable. Efforts have been made to prohibit the use of lead paint, but these have not proved successful.

**642. Lead Acetate $Pb(C_2H_3O_2)_2$.**—Lead acetate is perhaps the most important lead salt. It is prepared by boiling acetic acid and litharge in leaden pans and allowing the liquid to crystallise.

It is a white crystalline salt. It has a sweet taste and is therefore known as 'sugar-of-lead.' It is very soluble in water.

It finds a use in medicine, in dyeing as a mordant, and wherever a soluble lead salt is needed—in the laboratory or in the chemical work works.

Lead acetate forms two basic acetates when boiled with litharge

$$Pb(C_2H_3O_2)_2 + PbO + 2H_2O = Pb(C_2H_3O_2)_2 . Pb(OH)_2 . H_2O.$$

A solution of the dibasic acetate is employed in medicine as a lotion for the treatment of skin diseases.

**643. Lead Nitrate $Pb(NO_3)_2$** is prepared by the usual methods and forms white crystals. It is used in the laboratory to prepare nitrogen peroxide by the reaction

$$2Pb(NO_3)_2 = 2PbO + O_2 + 4NO_2.$$

For this purpose it has the advantage over other nitrates in that it has no water of crystallisation.

**643a. Lead Arsenate** is much employed as a spray for fruit-trees, designed to protect them against damage by caterpillars.

**644. Lead Sulphide PbS.**—Lead sulphide is found native as galena

(Plate XIV.). It may be made artificially by the action of hydrogen sulphide or a soluble sulphide on a solution of a lead salt,

$$Pb(C_2H_3O_2)_2 + H_2S = PbS + 2C_2H_4O_2.$$
$$Pb^{++} + S^{--} = PbS$$

It is a black solid, insoluble in water and in dilute acids, but is dissolved by hot concentrated hydrochloric acid (*v.* § 647). Nitric acid oxidises it to the nitrate and sulphate.

**645. Lead Sulphate $PbSO_4$** is one of the few insoluble sulphates. It is readily prepared by the addition of sulphuric acid to a solution of a soluble lead salt. It is used as a means of estimating lead gravimetrically.

**646. Lead Chromate $PbCrO_4$** is a useful pigment, known as chrome yellow. It is formed when a solution of a lead salt is mixed with a solution of a chromate. Lead chromate is a valuable yellow pigment and is much used for the cheaper yellow paints. It is not fully permanent, orpiment (arsenic trisulphide) being superior to it in this respect. When treated with lime a basic chromate, *chrome red*, results.

**647. Lead Chloride $PbCl_2$** is found native. It is readily prepared by the action of hydrochloric acid on lead oxide or carbonate, or by precipitation when a solution of a lead salt is mixed with hydrochloric acid.

Lead chloride is nearly insoluble in cold water (*c.* 1 : 100) but more soluble in boiling water (3 : 100). It is therefore readily crystallised and forms white silky needles. The solubility of lead chloride in hydrochloric acid is of interest. It is less soluble in moderately concentrated acid than in water, owing to the common ion effect (§ 118). With concentrated hydrochloric acid the lead ion forms a complex anion $PbCl_4^{--}$, and the salt dissolves more readily. The formation of this complex ion gives the reason why lead sulphide dissolves in concentrated hydrochloric acid (cf. §§ 120, 902). The chief interest of lead chloride is that it is one of the few sparingly soluble or insoluble chlorides, and thus its formation from cold solutions of lead salts and hydrochloric acid is characteristic of the metal and made use of in qualitative analysis.

**648. Lead Iodide $PbI_2$** is a golden-yellow salt, resembling the chloride in that it is nearly insoluble in cold water (1 : 1,000), but somewhat more soluble in boiling water. It forms a colourless solution.

**649. Basic Lead Salts.**—On diluting solutions of several lead salts or on boiling them with lead oxide basic salts are formed. Thus several basic lead chlorides, basic lead nitrates and basic lead acetates are all known.

**649a. Quadrivalent Lead Compounds.**—In addition to lead dioxide (already mentioned) and certain organic compounds, such as lead tetraethyl, the tetrachloride and tetra-acetate deserve some mention.

College.

If lead dioxide is dissolved in ice-cold concentrated hydrochloric acid, no chlorine is evolved. The deep yellow solution contains the acid $H_2PbCl_6$, and on addition to this of a concentrated solution of ammonium chloride a yellow salt, *ammonium plumbichloride* $(NH_4)_2PbCl_6$ separates

$$PbO_2 + 4HCl \rightleftharpoons PbCl_4 + 2H_2O$$
$$PbCl_4 + 2Cl^- \rightleftharpoons [PbCl_6]^{--}$$
$$2NH_4^+ + PbCl_6^{--} \rightleftharpoons [NH_4]_2[PbCl_6]$$

This salt is stable up to 115° C. and can be filtered off and dried.

When this salt is added to well-cooled concentrated sulphuric acid, lead tetrachloride separates as a yellow mobile liquid of density 3·18.

$$(NH_4)_2PbCl_6 + H_2SO_4 = (NH_4)_2SO_4 + 2HCl + PbCl_4.$$

It rapidly decomposes at room temperature to lead chloride and chlorine. In presence of water it forms lead dioxide and hydrochloric acid.

*Lead tetracetate* $Pb(C_2H_3O_2)_4$ is readily made by dissolving red lead in warm concentrated acetic acid. On cooling, white needles of the salt separate. Water hydrolyses it to lead dioxide; concentrated hydrochloric acid gives the tetrachloride. It is sometimes used as an oxidising agent in organic chemistry.

**650. Detection and Estimation of Lead.**—Lead salts are detected by their giving with hydrochloric acid a precipitate soluble in hot water but not in cold; and also by their giving with potassium chromate a vivid yellow precipitate of lead chromate (*q.v.*, § 646).

Lead is usually estimated by precipitating it as sulphate or chromate and weighing it as such.

## SUB-GROUP IV. A

**651. Sub-group IV. A of the Periodic Table.**—The elements of the sub-group IV. A, Titanium, Zirconium, Hafnium and Thorium, form a well-marked group. Their resemblance to silicon is noticeable, particularly in respect of their oxides, $TiO_2$, $ZrO_2$, $HfO_2$, $ThO_2$, which in the first three cases have some acidic properties and show a likeness to silica. The hydroxides, $Ti(OH)_4$, etc., form sols and gels like silicic acid. The metallic properties are not very well marked except in the case of thorium. While the elements themselves have a metallic lustre and electrical properties characteristic of metals, their compounds have the character of metalloids, the metallic character becoming more marked with increase of atomic weight. Thus the higher chlorides are volatile substances decomposed by water and the oxides have decided acidic properties.

The atomic structure of this group of elements is shown in the accompanying table :—

| Element. | Electronic groups of quantum number | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Titanium . | 2 | 8 | 10 | 2 | | | |
| Zirconium . | 2 | 8 | 18 | 10 | 2 | | |
| Hafnium . | 2 | 8 | 18 | 32 | 10 | 2 | |
| Thorium . | 2 | 8 | 18 | 32 | 18 | 10 | 2 |

The close resemblance in structure is notable. The structure resembles that of Group IV. B in that the outermost electrons consist of two pairs, but differs from it in that the atoms have an incomplete core and therefore present the phenomena of variable valency in a more marked degree.

## TITANIUM Ti, 47·90

**652. Occurrence.**—Titanium does not occur free. It is widely distributed in rather small quantities, but is chiefly found as rutile, impure titanium dioxide $TiO_2$, and ilmenite, ferrous titanate $FeTiO_3$. It is estimated that on account of its occurrence in igneous rocks, of which the greater part of the earth is composed, it is actually about the tenth commonest element.

**653. Preparation.**—Pure titanium dioxide is obtained by dissolving rutile in nearly concentrated sulphuric acid, the unstable titanic sulphate being formed together with ferrous and ferric sulphates. The mass is taken up in a little water, leaving most of the iron salts undissolved. On dilution titanic hydroxide is precipitated before the iron comes down. The hydroxide is washed free from iron with slightly acid water, dried and ignited.

The element titanium may be prepared by reducing titanium dioxide aluminothermically (§ 480), or better, by heating the liquid titanic chloride with sodium in a steel bomb of great strength,

$$TiCl_4 + 4Na = 4NaCl + Ti.$$

The element has little importance, but its alloy with iron *ferro-titanium* is used in making titanium steels, which have great resistance to wear. The alloy is made by melting iron and aluminium together and adding rutile to the mixture. The aluminium reduces this to titanium, which alloys with the iron,

$$4Al + 3TiO_2 = 2Al_2O_3 + 3Ti.$$

**654. Properties of Titanium.**—Titanium has a metallic lustre. Its density is about 4·5. It melts at about 2,000° C. The metal is ductile when pure, and it is a good conductor of electricity.

In its chemical properties it resembles silicon. Thus it burns in oxygen to titanium dioxide. At high temperatures it decomposes water, forming the oxide and hydrogen.

Acids do not attack the metal readily. Hot dilute sulphuric acid yields one of the lower sulphates and hydrogen. Nitric acid oxidises it to titanic acid $Ti(OH)_4$, or to titanium dioxide $TiO_2$. Concentrated sulphuric acid forms the unstable disulphate $Ti(SO_4)_2$ and sulphur dioxide.

**655. Valency of Titanium Compounds.**—Titanium forms three series of compounds in which it is divalent, tervalent and quadrivalent respectively. The first two are powerful reducing agents. The divalent and tervalent salts are coloured, a phenomenon typical of transition elements.

**656. Oxides of Titanium.**—The oxides TiO and $Ti_2O_3$ and the corresponding hydroxides exist. They are powerful reducing agents. The ordinary oxide is titanium dioxide $TiO_2$.

**657. Titanium Dioxide $TiO_2$** occurs native, as *rutile* (*brookite*, *anatase*). It is prepared in a pure state by the method described in § 653, above, and also by heating the native forms contaminated with iron titanate in a

mixture of hydrogen chloride and chlorine. Ferric chloride volatilises and passes on, leaving the pure titanium dioxide,

$$2FeTiO_3 + 4HCl + Cl_2 = 2FeCl_3 + 2TiO_2 + 2H_2O.$$

Titanium dioxide is a white powder when pure. It is very stable and is only reduced with great difficulty. Some acids attack it, but not readily, forming titanic compounds. When fused with alkalis titanates (*v.* § 658) are formed. Titanium dioxide is widely used as a white pigment—titanium white—which is quite non-poisonous and unaffected by hydrogen sulphide.

**658. Titanium Hydroxide, Titanic Acid, $Ti(OH)_4$ or $H_4TiO_4$.**—Titanic acid much resembles silicic acid. It is conveniently made by the action of alkalis on titanium tetrachloride.

$$TiCl_4 + 4NH_4OH = Ti(OH)_4 + 4NH_4Cl.$$

It forms a white precipitate.

Titanic acid can also, like silicic acid, be prepared as sols and gels.

Titanates are known, derived from orthotitanic acid $H_4TiO_4$, and also from metatitanic acid $H_2TiO_3$. Calcium titanate $CaTiO_3$ *perowskite*, is a not uncommon mineral, as is also *ilmenite* $FeTiO_3$. The titanates show a strong resemblance to the silicates.

**659. Titanium Halides.**—*Titanium fluoride* $TiF_4$ is known. It forms fluotitanates analogous to the fluosilicates (§ 603).

*Titanium Dichloride* $TiCl_2$, formed by the decomposition of titanium trichloride *in vacuo*, $2TiCl_3 = TiCl_2 + TiCl_4$, is a powerful reducing agent, as is also

*Titanium Trichloride* $TiCl_3$. This salt has a violet colour. The solid salt is prepared by passing a mixture of titanium tetrachloride and hydrogen through a heated tube,

$$2TiCl_4 + H_2 = 2TiCl_3 + 2HCl.$$

The violet solution of the salt obtained by electrolytic reduction of titanium tetrachloride finds a use in volumetric analysis as a direct means of titrating ferric iron. The solution has to be preserved from oxidation by the air in a piece of apparatus similar to that illustrated in Fig 89. When run into a solution of a ferric salt the titanium trichloride is oxidised and the iron reduced

$$Ti^{+++} + Fe^{+++} = Ti^{++++} + Fe^{++}$$

or

$$TiCl_3 + FeCl_3 = TiCl_4 + FeCl_2.$$

The end-point is found by taking out drops and mixing them with drops of sodium thiocyanate on a white tile. When all the ferric iron is reduced and the reaction is complete no red colour is produced. Titanous chloride is used for estimating many other oxidising agents.

*Titanium Tetrachloride, Titanic Chloride* $TiCl_4$.—This substance is prepared by passing chlorine over a mixture of titanium dioxide and carbon.

$$2Cl_2 + TiO_2 + C = TiCl_4 + CO_2.$$

The chloride volatilises and is condensed. It should be redistilled to remove ferric chloride derived from iron present in the oxide.

Titanium tetrachloride is a heavy colourless mobile liquid boiling at 135° C. It fumes in air and when mixed with water gives basic chlorides and finally orthotitanic acid (cf. stannic chloride).

$$TiCl_4 + H_2O \rightleftharpoons TiCl_3(OH) + HCl$$
$$TiCl_3(OH) + H_2O \rightleftharpoons TiCl_2(OH)_2 + HCl, \text{ etc.}$$

In presence of sufficient hydrogen chloride little dissociation takes place and crystalline hydrates can be prepared.

Its properties are, on the whole, less like those of a metallic chloride than are those of stannic chloride, and more metallic in character than those of silicon tetrachloride.

**660. Oxy-salts of Titanium.**—The sulphate of trivalent titanium $Ti_2(SO_4)_3$ exists and forms red and violet alums with rubidium and cæsium sulphates. Titanic sulphate has not been obtained pure, but a titanyl sulphate $(TiO)SO_4$ is known. It is doubtful if any other oxy-salts exist, except possibly phosphates.

**661. Detection.**—A titanic compound, such as titanic sulphate, gives with hydrogen peroxide a deep orange colour due to pertitanic acid $H_4TiO_5$,

$$Ti(SO_4)_2 + 4H_2O \rightleftharpoons Ti(OH)_4 + 2H_2SO_4$$
$$Ti(OH)_4 + H_2O_2 \rightleftharpoons TiO(OH)_4 + H_2O.$$

The reaction serves also as a test for hydrogen peroxide.

## ZIRCONIUM Zr, 91·22

Zirconium is not by any means a rare element, being widely distributed in the rocks of the earth's crust. It is found in the form of the dioxide zirconia and also as zirconates. Zirconium silicate, *zircon*, is also found.

**662. Preparation of the Element.**—Pure zirconia may be reduced to the metal by heating it with calcium,

$$2Ca + 2ZrO_2 = CaZrO_3 + Zr + CaO.$$

**663. Properties of Zirconium.**—Zirconium exists in two forms, amorphous and crystalline. Crystalline zirconium is hard and brittle and has a metallic lustre. It melts at about 1,700° C. Its conductivity is about that of iron. Its physical properties are then those of a metal.

In its chemical properties zirconium strongly resembles silicon. Heated in oxygen it burns at high temperatures, forming zirconia $ZrO_2$. Both zirconium and titanium readily form nitrides.

Acids, in general, have little effect upon zirconium, but hydrofluoric acid readily forms the tetrafluoride $ZrF_4$.

**664. Zirconium Dioxide $ZrO_2$.**—Zirconium dioxide, zirconia $ZrO_2$, is found native as *baddeleyite*. Its properties resemble those of silica in many respects. It is hard, very infusible, and non-volatile, and has a low coefficient of expansion.

The crystalline material is very stable and is attacked only very slightly by acids other than hydrofluoric. The amorphous material made by heating the hydroxide dissolves fairly readily in acids.

*Zirconium hydroxide* $Zr(OH)_4$ is readily made by the action of ammonia on zirconium salts. It can be obtained as sols and gels. It is amphoteric, giving salts with acids and zirconates with alkalis.

The *zirconates* are mostly mixed oxides rather than true salts.

**665. Salts of Zirconium.**—Three chlorides are known, $ZrCl_2$, $ZrCl_3$, $ZrCl_4$, but only the last has any importance.

*Zirconium tetrachloride* is made by the action of chlorine and sulphur chloride on heated zirconium silicate (*zircon*). The tetrachlorides of zirconium and silicon are found and are separated by distillation.

Zirconium chloride forms white fuming crystals volatile at 300° C. In solution it hydrolyses to the oxychloride $ZrOCl_2.H_2O$.

$$ZrCl_4 + H_2O = ZrOCl_2 + 2HCl.$$

Several zirconium sulphates exist, but most of them appear to be basic zirconyl compounds of the type $ZrOX_2$. The normal sulphate $Zr(SO_4)_2$ is, however, known and forms an insoluble double sulphate with potassium sulphate. This affords a test for zirconium.

*Zirconium silicate* $ZrSiO_4$ forms the mineral *zircon* or *jargoon*. It forms hard crystals of brilliant lustre, which are often of a fine blue tint, when they have a value as gem stones. The colourless varieties, not unlike diamond, are known as 'Matura diamonds.' They are, of course, less hard than diamond (hardness 7·5, about equal to quartz) and less lustrous (refractive index of zircon 1·99 : of diamond 2·42), though much superior to any artificial diamonds in this respect.

Other oxy-salts of zirconium (nitrate, oxalate, phosphates) exist, but are for the most part zirconyl compounds, such as $ZrO(NO_3)_2$, $ZrO(C_2O_4)$, etc.

Zirconium is thus definitely of metalloid character, resembling a metal in physical properties but showing a tendency to non-metallic properties in the instability of its salts.

## HAFNIUM Hf, 178·6

This element is a new-comer, being discovered as lately as 1922. It owes its discovery to the work of Moseley (§ 142) and to the Bohr theory of atomic structure. Moseley showed by his study of X-ray spectra that an element of atomic number 72 was missing. The Periodic table in that neighbourhood ran :—

| | |
|---|---|
| 69. Thulium. | 72. ——— |
| 70. Ytterbium. | 73. Tantalum. |
| 71. Lutecium. | 74. Tungsten. |

Urbain, as a result of investigation of some rare-earths, found a rare-earth element, which he called 'celtium' and believed to fill the space 72. Moseley showed by the X-ray spectra that this was a mixture, but later investigators found traces of a line corresponding to 72, and concluded that 'celtium' was really the missing element 72. Bohr's theory of the rare-earths indicated that the last of them must be lutecium (71), and that element 72 would not be a rare-earth (2, 8, 18, 33, 9, 2) but an analogue of zirconium (2, 8, 18, 32, 10, 2). Thus :—

STRUCTURE OF ELEMENTS 69–74, ACCORDING TO BOHR.

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| 40. Zirconium . . | 2 | 8 | 18 | **10** | **2** | |
| 69. Thulium . . | 2 | 8 | 18 | 30 | 9 | 2 |
| 70. Terbium . . | 2 | 8 | 18 | 31 | 9 | 2 |
| 71. Lutecium . . | 2 | 8 | 18 | 32 | 9 | 2 |
| | | End of | rare eart | h group | | |
| 72. ——— | 2 | 8 | 18 | 32 | **10** | **2** |
| 73. Tantalum . . | 2 | 8 | 18 | 32 | 11 | 2 |
| 74. Tungsten . . | 2 | 8 | 18 | 32 | 12 | 2 |

Urbain's celtium, if it existed, was clearly a rare-earth element, all of which, according to Bohr, were already known, except the element 61, which for other reasons could not be identified with celtium. Bohr suggested that zirconium ores should be examined to find out if they gave X-ray spectra corresponding

to the presence of an element of atomic number 72. Coster and Hevesy examined the ores and it turned out that some zirconium minerals contained as much as 15 per cent. of hafnium, as the new element was called, while all zirconium minerals contained about 0·15 per cent., a fact accounting for the considerable difficulty which had been found in obtaining consistent results for the atomic weight of zirconium !

The new element was found to be extremely like zirconium, and was only separated by a lengthy process of fractional crystallisation. The fluorides of both zirconium and hafnium form stable zirconifluorides and hafnifluorides, such as $(NH_4)_2ZrF_6$ and $(NH_4)_2HfF_6$. These were fractionally crystallised, the X-ray spectrograph (§ 142) being used to test the degree of separation obtained.

**666. Properties of Hafnium and its Compounds.**—Hafnium and its compounds show a likeness to zirconium which is only paralleled by the similarity of the rare-earth elements, the only appreciable difference being in physical properties such as the densities, melting points and solubilities of its compounds.

## THORIUM Th, 232·12

**667. History and Occurrence.**—The oxide thoria has been known since 1828. Thorium is widely distributed. Its chief ores are *thorite* and *orangite*, in which thorium dioxide is associated with silica and some uranium. The chief source of the element is *monazite sand*, a mixture of the phosphates of various rare-earths. Thorium oxide is important commercially as the chief constituent of incandescent mantles. The compounds of thorium have a further interest as being radioactive. Thorium and its compounds are very feebly radioactive, but some of its degradation products are of high activity (Chapter XXVI).

**668. Preparation and Properties of Thorium.**—Thorium may be prepared by the action of sodium on the chloride.

Thorium is an iron-grey heavy metal, of high melting point. It is but slightly attacked by acids. The metal has found no practical uses.

**669. Thorium Dioxide $ThO_2$** is the only known oxide of thorium. The valency of thorium, unlike that of the other metals of the group, is always four.

It is prepared from monazite, which contains the phosphates of thorium and the rare-earths. The monazite having been freed by an electromagnetic separator (*v.* § 1011) from extraneous minerals is dissolved in concentrated sulphuric acid. The material is diluted and alkali cautiously added. Thorium phosphate is the first substance to be precipitated. This is converted into thoria by fusion with sodium carbonate or by other secret processes.

Thoria forms a white powder of great stability. Acids and reducing agents attack it only with great difficulty. The hydroxide $Th(OH)_4$ is made by the usual methods. It is basic in character and readily dissolves in acids. The chief use of thoria is in incandescent mantles.

The principle of the incandescent mantle is that a solid at a

given temperature emits much more light than a gas. The oxy-hydrogen flame gives little light, but a piece of lime placed in it glows brilliantly. Mantles of platinium gauze were first tried, but the prolonged heating damaged them. It was then noticed that the oxides of the rare-earths glowed particularly brightly. Auer von Welsbach tried a number of these oxides and finally found thoria the most suitable. Curiously, the thoria gives a very poor light unless it contains some 1 per cent. of ceria—a phenomenon not satisfactorily explained.

Incandescent mantles are made in various ways. A usual method consists of weaving the mantles as a continuous ' hose ' from *ramie* fibre, a silk-like material obtained from a plant, or sometimes from artificial silk.

This ' hose ' is soaked in a solution of thorium and cerium nitrates together with the nitrates of certain other metals (Mg, Al, Be), the oxides of which give strength to the mantle. Excess of liquid is squeezed out and the hose cut into suitable lengths and dried on forms to preserve the shape. The head of the mantle is strengthened with magnesium and aluminium nitrates and sewn into shape with asbestos thread. The cotton is burnt away in a high temperature flame and the skeleton of mixed oxides which is left is strengthened by being dipped in collodion, which gives the mantle strength enough for packing and transit.

Sometimes a mixture of thick collodion with thorium and cerium nitrates is squirted into fine threads, which are then woven into mantles.

**670. Salts of Thorium**—*Normal thorium carbonate* does not exist, but basic carbonates are known.

*Thorium nitrate* $Th(NO_3)_4$ is obtained by the action of nitric acid on thoric hydroxide. It forms very deliquescent white crystals with the usual properties of nitrates.

*Thorium sulphate* $Th(SO_4)_2$ is made by the action of sulphuric acid (2 : 1) on thoria. It dissolves unchanged in cold water, but hot water alters it to ' thoryl ' sulphate $ThO(SO_4)$.

*Thorium tetrachloride* $ThCl_4$ is made by the action of chlorine on a mixture of thoria and carbon,

$$ThO_2 + C + 2Cl_2 = ThCl_4 + CO_2.$$

Thorium tetrachloride has much more of the character of a metallic salt than the chlorides of titanium, etc. It forms white crystals, which volatilise when heated. It dissolves in water freely and forms hydrates It does not appear to be markedly hydrolysed by cold water.

The radioactive properties of thorium are discussed in Chapter XXVI.

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# CHAPTER XVII

## NITROGEN

**671. General.**—The element nitrogen, though in the free state decidedly unreactive, has a large number of interesting compounds. It forms a part of many organic compounds, and, since these include the essential substances always present in living matter, a supply of nitrogen in a form available to plants is the most important concern of agricultural chemistry. The methods of rendering atmospheric nitrogen available to plants are further discussed under the headings of Ammonia and Nitric Acid.

The structure of the nitrogen atom is characterised by the presence of 5 electrons in the outermost group, and in consequence its maximum positive and negative valencies must be 3 and 5 respectively.

The valency of 5 only appears in nitrogen pentoxide, nitric acid and its derivatives. In the remainder of its compounds nitrogen has normally a valency of 3, sometimes of 4.

The element is classified in the Periodic table with phosphorus, arsenic, antimony and bismuth, but although the group as a whole shows well-marked common properties, nitrogen, as is usual with the first member of a group, shows less resemblance to the type than do the remainder. The stability of its hydride (ammonia) and of the compounds containing the amino group — $NH_2$, mark it off from phosphorus and the remainder of Group V. B. The group as a whole is further discussed in §§ 757, 842.

**672. History.**—Nitrogen was probably first recognised as a distinct gas by D. Rutherford in 1772, who prepared it by removing oxygen from the air by processes of combustion. He caused phosphorus, charcoal, etc., to burn in air and removed the products of combustion with alkalis. Lavoisier recognised its elementary nature and called it ' azote,'[1] while Chaptal, in 1823, propounded the name nitrogen.[2]

**673. Occurrence.**—Nitrogen is found in the free state in the atmosphere, and it constitutes 78·06 per cent. by volume or 75·5 per

[1] The name ' azote ' is derived from the Greek *a*, not, and *ζωή*, *zoe*, life, implying that it is the part of the air which does not support life.

[2] The name nitrogen means a substance which produces saltpetre or nitre; the Greek word, *νίτρον*, *nitron*, was believed by Chaptal to represent nitre, though in fact the Greek *νίτρον* was clearly sodium carbonate. The second half of the word is the Greek *γεννάω*, I produce.



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cent. by weight of dry air. It is also present in solution in all natural waters.

Combined nitrogen is present in all living matter, and in most of its products. The soil contains always a small proportion of nitrogen as organic matter, ammonium compounds, nitrites and nitrates, and thus most surface water also contains traces of nitrogen compounds. Few minerals contain appreciable amounts of combined nitrogen, the only mineral source of which is the extensive deposits of sodium nitrate in Chili.

**674. Nitrogen Circulation in Nature.**—Nitrogen is a constituent of the protoplasm which is the essential living constituent of both animals and plants. The framework :—muscles, skin, hair and

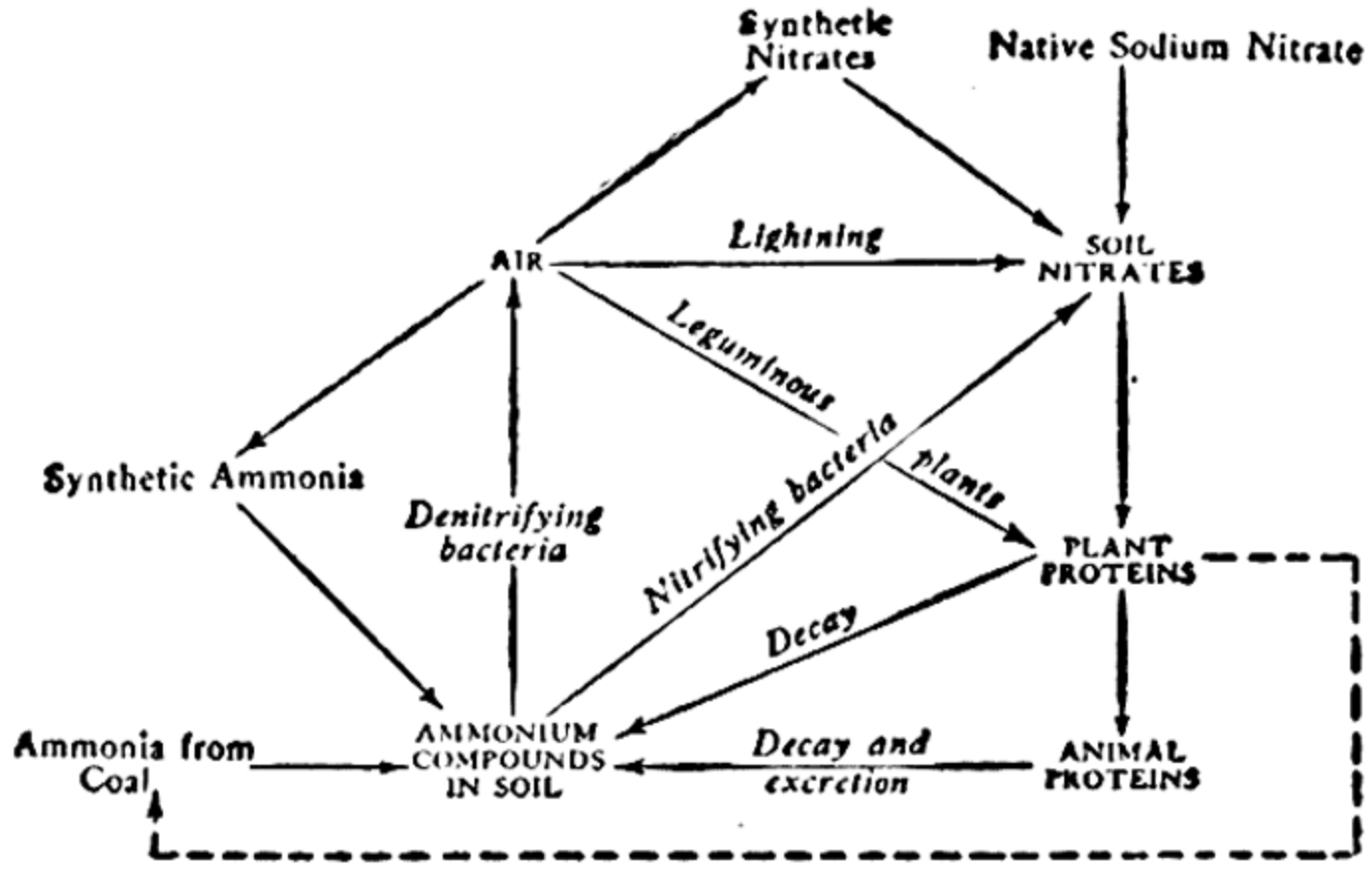


FIG. 125.—Nitrogen circulation and sources.

connective tissue—of animals also contains a high percentage of combined nitrogen. The animal is not able to assimilate free nitrogen, but obtains its nitrogen by eating plants or other animals. Plants cannot assimilate free nitrogen, but as a rule build up their nitrogen compounds from the nitrates present in small quantity in the soil. In a state of nature, then, combined nitrogen is continually being taken from the soil and transferred to the bodies of animals and plants. When these die, they decay, which means that they are assimilated by bacteria which break down the complex protein molecules into simple compounds. As a consequence of this process, the nitrogen becomes once more transferred to the soil in the form of ammonium compounds. The *nitrifying bacteria*, always present in the soil, oxidise these to nitrates which are then again available to plants.

If this were the whole story, no nitrogen would be lost, and no supply would be needed. There are, however, present in the soil certain *denitrifying bacteria* which cause a loss of combined nitrogen

by oxidising the ammonium compounds formed by decay to free nitrogen. This loss is normally balanced in two ways. Firstly, every flash of lightning causes the nitrogen and oxygen of the air along its track to combine. Nitric acid (§ 737) is thus formed, and the rain of a thundershower thus supplies some combined nitrogen to the soil. In the second place, certain leguminous plants, *e.g.*, lupins, vetches, etc., harbour in nodules on their roots certain bacteria which have the remarkable property of causing free nitrogen to combine and form products which the plant can assimilate.

In a state of nature these processes strike a balance, and nitrogen neither accumulates nor is depleted. Man, however, takes crops from the soil, eats them, and excretes their nitrogen compounds into the sewers and thence to the sea. The fields become impoverished in nitrogen, and if good crops are to be obtained, fresh nitrogen compounds must be supplied. This is done by using artificial fertilisers. Chief among these are (i.) ammonium salts from coal—the nitrogen of ancient forests; (ii.) sodium nitrate from Chili, possibly deposits formed by the decay of seaweeds; (iii.) ammonium salts obtained synthetically from the air (§ 689); (iv.) nitrates obtained synthetically from the air (§ 737); (v.) cyanamide obtained synthetically from air, coke and limestone (§ 580 *b*).

The air offers a practically unlimited supply of nitrogen, and there is now little reason to fear a shortage.

**675. Composition of Air.**—Air is an extremely complex mixture. The gases nitrogen, oxygen, and the inert gas argon (Ch. XXV.), are always present, and make up together about 99·9 per cent. of dry air. If the traces of other gases are neglected, a typical analysis would be :—

| | By Weight. | By Volume. |
|---|---|---|
| Nitrogen . . . | 75·5 | 78·06 |
| Argon . . . | 1·3 | 0·94 |
| Oxygen . . . | 23·2 | 21·0 |
| | 100·0 | 100·00 |

In addition to these gases there is present in normal air about 1 per cent. of water-vapour by volume. This figure may fall to much lower values in dry and very cold areas, and rise to as much as 4 per cent. in humid tropical climates. The effects of the moisture of the air are further discussed under the heading of Water (§ 209).

There is also in the atmosphere a small proportion of carbon dioxide (*q.v.*) which amounts to about 3 volumes per 10,000 volumes

of air (0·03 per cent.). This figure may rise to 8 volumes in still, foggy weather in towns, and to higher values in ill-ventilated rooms.

Since all gases which are set free enter the air, the latter contains, in addition to the gases mentioned, small traces of a great number of gases, notably ammonia, oxides of nitrogen, hydrogen, hydrocarbons, sulphur dioxide, hydrogen sulphide, ozone, volatile organic compounds, and the rare gases, helium, krypton, neon and xenon. These gases do not exhaust the chemical possibilities of the atmosphere, for air contains immense numbers of floating dust particles (in London about 100,000 per cubic centimetre). These consist of carbon from smoke, organic matter, mineral dust, etc. Near the sea there is always a proportion of sodium chloride in the air, probably as wind-borne dust resulting from dried spray.

**676. Air a Mixture.**—Until the beginning of the nineteenth century air was often thought to be a chemical compound of oxygen and nitrogen. There is little in favour of such a view except its apparently constant composition. The evidence against it falls under the following headings :—

(*a*) The composition of air is not entirely constant, small variations of the proportions of oxygen and nitrogen being found.

(*b*) The properties of air are precisely those which would be expected of a mixture of nitrogen and oxygen, whereas a chemical compound always possesses properties different in some respects from those of its constituents.

(*c*) The nitrogen and oxygen can be separated by diffusion (§ 54) ; and by solution in water, in which oxygen is more soluble than is nitrogen.

(*d*) When nitrogen and oxygen are mixed in the correct proportions a substance indistinguishable from air is produced, without any change of temperature or volume or other sign of chemical change.

(*e*) The formula of air, if a compound, would be approximately $N_{15}O_4$, and a gas of this formula should have a density about ten times as great as that which air actually manifests.

**677. Preparation of Nitrogen.**—Nitrogen is prepared (1) by removal of oxygen, etc., from the air by chemical or physical means ; (2) by the decomposition of nitrogen compounds.

Both of these methods have been employed in the laboratory, but the latter is considerably the more convenient. On the industrial scale nitrogen is invariably prepared from the air by methods (pp. 501–2) which are not available on the laboratory scale.

**678. Preparation of Nitrogen from the Air.**—Nitrogen is prepared from the air either by chemically absorbing oxygen, carbon dioxide, etc., or by liquefying the air and resorting to a process of fractional distillation.

In the laboratory we may prepare nitrogen in a state of comparative purity by bringing air into prolonged contact with sodium pyrogallate solution. The oxygen and carbon dioxide are rapidly removed and the residual nitrogen contains only some 1 per cent. of argon. The reaction is, however, too slow to allow of the continuous preparation of nitrogen by bubbling air through sodium pyrogallate in any ordinary form of gas-washing bottle.

Air, however, may be passed over a heated metal, copper gauze or finely-divided iron, carbon dioxide and water vapour being previously removed by means of caustic potash and concentrated sulphuric acid. Care must be taken that the stream of air is passed over the metal at such a rate that no oxygen remains unabsorbed.

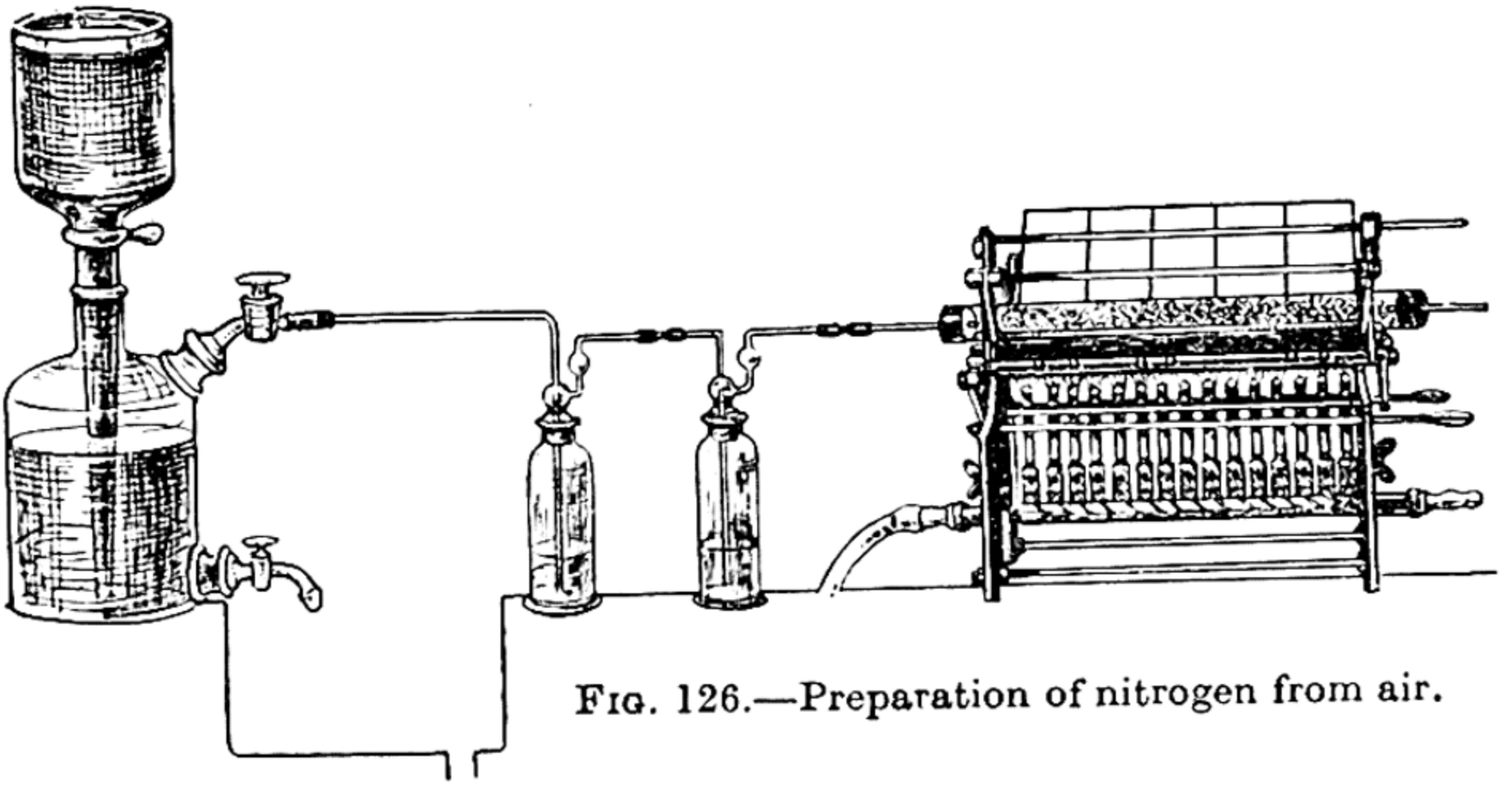

FIG. 126.—Preparation of nitrogen from air.

Numerous commercial adaptations of this method have been proposed. Among them may be mentioned the extraction of nitrogen from furnace gases. The gases from the properly-regulated combustion of coke contain nitrogen, carbon dioxide and a little carbon monoxide. The furnace gases are passed over a mixture of heated copper and copper oxide to remove any residual oxygen, and at the same time to oxidise any carbon monoxide. The carbon dioxide is then absorbed by caustic soda, or by water under pressure, and nitrogen remains.

The burning of a mixture of air and hydrogen (which is a by-product from various electrolytic processes (*e.g.* § 230) has also been used to prepare nitrogen.

A third process for the extraction of nitrogen from air depends on the liquefaction of air and its subsequent fractional evaporation. The boiling point of liquid nitrogen is — 195° C., and of liquid oxygen — 182·5° C. This small difference is sufficient to allow of a

separation of the gases, nitrogen of 99·5 per cent. purity being obtained. When a mixture of two liquids is allowed to evaporate, the vapour contains a greater proportion of the more volatile substance, and the residual liquid a less proportion than was contained in the liquid before evaporation. A complete separation cannot, however, be obtained in this way, and the gas obtained by evaporating liquid air still contains about 10 per cent. of oxygen. It is necessary, therefore, to use the principles of the rectifying column to obtain pure nitrogen.

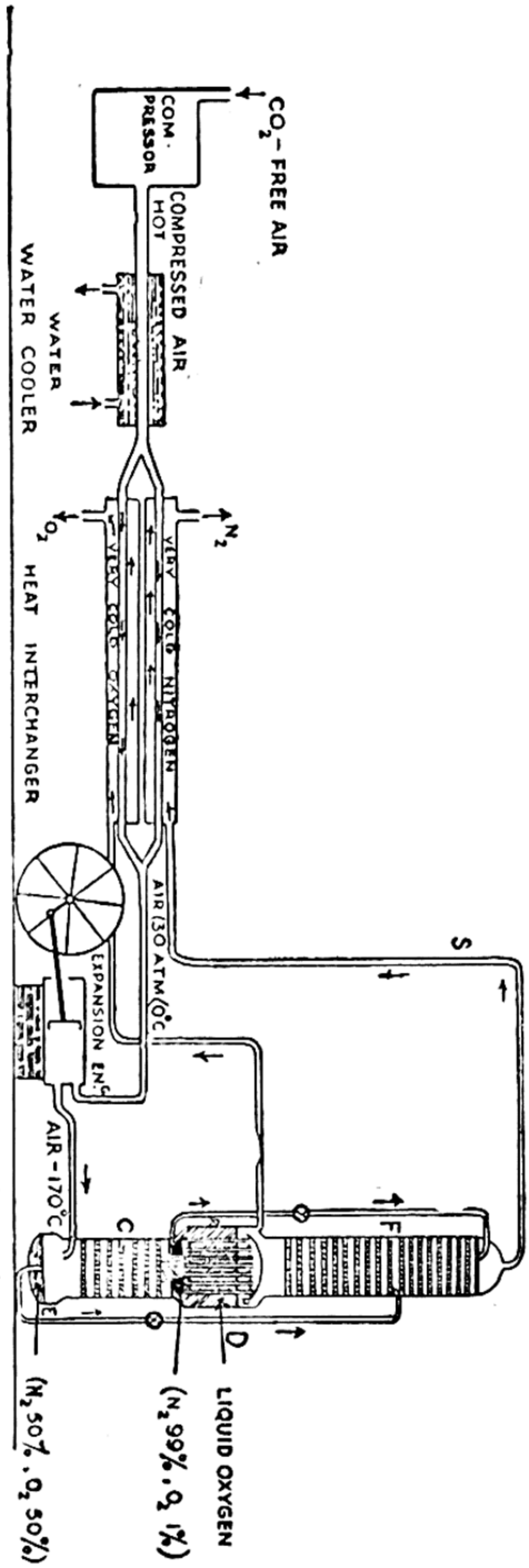


Fig. 127.—Diagram of plant for separation of oxygen or nitrogen from air.

The most modern plants employ the Claude system of air-liquefaction coupled to the Linde oxygen column.

The air is freed from carbon dioxide with lime or caustic soda, and a compressor then compresses the air to about 30 atm. This process causes it to become hot and the heat is removed by water-cooling. It is then further cooled by a heat-interchanger, consisting of concentric tubes through one of which the gas passes. The other carries the exceedingly cold oxygen or nitrogen leaving the apparatus. These cool the gas and freeze out any moisture. The compressed air is then used to work an expansion engine,[1] which is coupled to a dynamo. The expansion engine restores a part of the power used in the compression of the gas. The gas does work by its expansion from 30 atm. to 4 atm., and this work is obtained at the expense

[1] No cylinder lubricant is used, for it is found that dry fat-free leather packing is the most satisfactory way of avoiding leakage.

of its heat-energy. Consequently the temperature of the air falls to very little above its liquefaction point. This cold air is then led into a Linde oxygen column (Fig. 128). It passes upward through a series of plates over which liquefied air, rich in oxygen, is trickling. This liquid air is evaporated to some extent by the incoming air, and so becomes richer in oxygen, finally collecting at E. This liquid air then contains 50–60 per cent. of oxygen. The incoming air passes upward and has most of its oxygen condensed out by the down-flowing air. It then reaches the nest of tubes D, which are immersed in the finally produced liquid oxygen. The air at 4 atm.[1] partly liquefies at the temperature of boiling oxygen. The first part liquefied contains about 40 per cent. of oxygen and trickles back through the shelves, C to E. The gas which is not liquefied in the early stages contains only about 1 per cent. of oxygen. The gas finally condenses in the last of the tubes D traversed as nearly pure liquid nitrogen, and is led from thence to the top of the upper rectification column. The liquid air, rich in oxygen, from the bottom of the column E is led in half-way up the column. The liquid nitrogen (1 per cent. $O_2$ only) running down the column evaporates and pure nitrogen comes off, the small proportion of oxygen passing to the base of the column. The liquid flowing down from F evaporates, producing much nitrogen gas and little oxygen: this little oxygen is condensed again as it rises by the evaporating nitrogen. This liquid oxygen, growing ever richer, flows down to the reservoir R, while gaseous nitrogen, becoming ever purer, passes upward to the exit and so to the heat exchanger. The gas evolved by the evaporating oxygen at R is led off through the pipe S to the heat exchanger and finally compressed into cylinders.

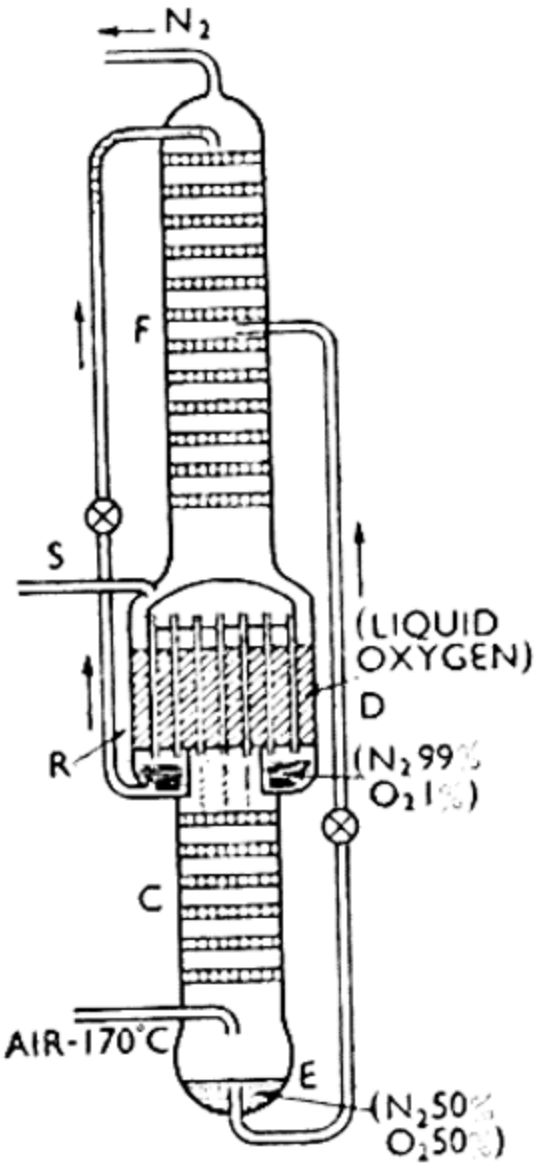


FIG. 128.—Linde oxygen column.

Summarising the processes:

(i.) Air is freed from $CO_2$, compressed to 30 atm. and cooled to *c.* 15° C.

(ii.) The compressed air passes through a heat exchanger, where the outflowing gases cool it further.

(iii.) The compressed air does work in an expansion engine and so is cooled to near its liquefaction point.

(iv.) This cold air is liquefied by the action of boiling oxygen. The air first liquefied is rich in oxygen and 'scrubs' the incoming air so that a portion (E), containing 50 per cent. of oxygen, remains as liquid while a part containing 1 per cent. of oxygen passes on and is also liquefied.

(v.) The liquid nitrogen (1 per cent. $O_2$), passes down a column from the top and pure $N_2$, which passes off, evaporates from it.

(vi.) The 50 per cent. oxygen (E) passes into the column half-way up and evaporates off its nitrogen and condenses any oxygen in the issuing nitrogen. Pure liquid oxygen collects in R and evaporates.

(vii.) The cold purified gases return to the heat exchangers.

[1] Air at 1 atm. pressure would not liquefy at the temperature of boiling oxygen; air at 4 atm. has a higher boiling point and therefore liquefies.

**679. Chemical Methods of Preparing Nitrogen.**—These methods all depend on the oxidation of ammonia or ammonium compounds, and comprise :—

(1) The decomposition of the ammonium salts of certain strongly oxidising acids.

(2) The action of strong oxidising agents on ammonia.

(1) *Preparation from ammonium salts.*—The simplest method of making nitrogen is by heating ammonium nitrite, or, preferably, a mixture of ammonium chloride and sodium nitrite.

If 1 part of each of the above and 5 parts of water are steadily heated in a round-bottomed flask fitted with a safety tube, nitrogen is evolved. Ammonium nitrite is first formed,

$$NH_4^+ + NO_2^- \rightleftharpoons NH_4NO_2,$$

and then decomposes,

$$NH_4NO_2 = N_2 + 2H_2O.$$

The use of the two salts is preferred to that of pure ammonium nitrite which is unstable and cannot be long preserved at ordinary temperatures. The nitrogen contains traces of ammonia and oxides of nitrogen and may be purified by passage through a mixture of saturated potassium dichromate solution and sulphuric acid.

A less convenient method of preparing the gas is the action of heat on ammonium dichromate,

$$(NH_4)_2Cr_2O_7 = N_2 + 4H_2O + Cr_2O_3,$$

which is an unduly vigorous reaction.

(2) *Preparation from ammonia.*—If a concentrated solution of ammonia be placed in a three-necked Woulffe's bottle and chlorine be led in, the reaction

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$$

takes place and nitrogen is evolved. The nitrogen is washed with water to remove any excess of ammonia and ammonium chloride fumes, and is then collected over water. It is essential that excess of ammonia shall be present in order to avoid the formation of the highly explosive nitrogen trichloride, $NCl_3$ (*q.v.*, § 753). The method is much less convenient than that already described.

Bleaching powder readily oxidises ammonia. If a thin cream of bleaching powder and water is mixed with concentrated ammonia solution, large quantities of nitrogen are evolved on warming,

$$3CaOCl_2 + 2NH_3 = N_2 + 3H_2O + 3CaCl_2.$$

If very pure nitrogen is required for quantitative work it is best

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prepared by leading nitric oxide (from nitric acid and copper through ammonia solution. The resulting mixture of ammonia and nitric oxide is passed over red-hot copper gauze, when the reaction

$$4NH_3 + 6NO = 5N_2 + 6H_2O$$

takes place. Excess of either gas and any other impurities are removed by successive passage through dilute sulphuric acid, fused potash, concentrated sulphuric acid and finally again red-hot copper gauze.

The effect of heat upon sodium azide $NaN_3$ has been used to prepare very pure nitrogen. The substance decomposes when heated, leaving behind metallic sodium,

$$2NaN_3 = 2Na + 3N_2.$$

**680. Physical Properties of Nitrogen.**—Nitrogen is a colourless gas without taste or smell. It is not poisonous, but does not, of course, support life. The gas is somewhat lighter than air. (Density = 14·01. Density of air = 14·4). It is liquefied on cooling to a colourless liquid, which boils at − 195° C., and freezes to a solid at − 210° C. Nitrogen is sparingly soluble in water, 100 volumes of which dissolve 2·3 volumes at 0° C.

**681. Active Nitrogen.**—When nitrogen is submitted to the action of the electric discharge at low pressures, a yellow glow appears which persists for a little time. At the same time the chemical properties of the gas are profoundly altered, a part of the nitrogen becoming highly reactive, combining directly with non-metals, such as sulphur, iodine, phosphorus and with almost all metals.

These remarkable phenomena have proved very difficult of explanation. The suggestion that a molecule, $N_3$, similar to ozone $O_3$ (cf. pp. 612 seq.) is produced, is disproved by the character of the spectrum and the fact that the active form cannot be condensed out by liquid air. A triatomic form of nitrogen would certainly boil at a higher temperature than the ordinary diatomic form.

The suggestion that active nitrogen is atomic nitrogen N is supported by several facts, but as the amount of energy needed to activate the nitrogen is much less than that needed to dissociate it into atoms, this theory is in doubt. Probably active nitrogen consists of ' metastable ' molecules, the atoms of which are so arranged as to have a greater amount of available energy than ordinary molecular nitrogen, together with a small proportion of free nitrogen atoms which combine to form molecules, releasing energy in doing so. The metastable molecules are responsible for the chemical activity and the atoms for the glow, the spectrum of which indicates that it is derived from atomic nitrogen.

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**682. Chemical Properties.**—At temperatures below 200° C. nitrogen is quite unreactive. At a dull red heat and above, however, many of the metals form *nitrides* in which the valency of the metal is normal and nitrogen is tervalent. Thus magnesium, heated in nitrogen, forms the magnesium nitride $Mg_3N_2$,

$$3Mg + N_2 = Mg_3N_2.$$

If magnesium powder be heated to redness in a covered crucible for some time and allowed to cool, the lower part of the residue will consist mainly of the nitride. Lithium, calcium, aluminium and the rare-earth metals readily form such nitrides.

These nitrides are readily decomposed by water, giving ammonia,

$$Mg_3N_2 + 6H_2O = 2NH_3 + 3Mg(OH)_2.$$

Nitrogen also reacts with oxygen, hydrogen, silicon and carbon.

Nitrogen reacts with oxygen at high temperatures, nitric oxide being formed,

$$N_2 + O_2 \rightleftharpoons 2NO - 43{\cdot}2 \text{ Cals.}$$

The reaction is endothermic and therefore the greatest proportion of nitric oxide is formed at very high temperatures. The process for producing nitric acid from the air, described in § 737, is based on this reaction, the details of which are there further discussed.

With hydrogen, ammonia is formed. The yield is inconsiderable, except under the highest pressures and in presence of suitable catalysts.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 23{\cdot}8 \text{ Cals.}$$

This reaction is exothermic and is also accompanied by a diminution of volume. For this reason, the manufacture of ammonia by this method (§ 689) is conducted at comparatively low temperatures, and at the highest pressures available.

Nitrogen and carbon react to a small extent when an arc is struck between carbon poles in an atmosphere of nitrogen, cyanogen $C_2N_2$ being formed.

$$2C + N_2 = C_2N_2.$$

Silicon and boron form nitrides when heated in an atmosphere of nitrogen.

**683. Commercial Uses.**—Nitrogen is chiefly used in the manufacture of calcium cyanamide, ammonia and nitric acid. Other minor uses are in filling gas-filled electric lamps and high temperature thermometers, and in general it finds a use where an unreactive gas is required.

**684. Formula and Atomic Weight.**—That the molecule of nitrogen contains at least two atoms is shown by the fact that two volumes of ammonia, when treated with chlorine or exploded with oxygen,

yield 1 volume of nitrogen. The ratio of the specific heats of nitrogen at constant pressure and constant volume is 1·408 at 0° C., which also indicates that it is a diatomic gas.

The atomic weight of nitrogen is shown by the molecular weights of its many volatile compounds to be approximately 14·0. The best determination of its atomic weight is probably that of Richards (§ 70), but other very accurate determinations have been made. The chief methods employed have been the measurement of the density of very highly purified nitrogen, and the determination of the proportion of nitrogen in the oxides of nitrogen. The principle of the latter method is the exact weighing of a quantity of the oxide of nitrogen in a closed vessel, containing an iron or nickel-wire spiral capable of being heated electrically from the exterior of the vessel. By heating the spiral the oxide is decomposed,

$$4N_2O + 3Fe = Fe_3O_4 + 4N_2,$$

and the increase of weight of the iron wire gives the weight of oxygen in the already known weight of oxide of nitrogen. In a certain experiment, 5·6269 gms. of nitrous oxide yielded 2·0454 gms. oxygen. Hence the ratio, $N_2O : O = 44{\cdot}015 : 16$, and

$$N = \frac{44{\cdot}015 - 16}{2} = 14{\cdot}008.$$

The latter figure is taken to be correct as the result of the agreement of several sets of determinations carried out by different methods.

Very accurate determinations of the density of nitrogen have been made by Guye's Limiting Density Method (§ 65). Since Avogadro's law is only true for 'perfect' gases, the density of a gas at N.T.P. does not give an absolutely exact measure of its molecular weight. It is possible, however, to measure the compressibility of the gas and thus calculate with accuracy the density the gas would have if it were a perfect gas and followed Boyle's law with complete accuracy. The density so obtained gives values for the atomic weight which are comparable in accuracy with the best chemical determinations. There are two isotopes $^{14}N$ and $^{15}N$, the latter being present to the extent 0·6 per cent.

**685. Detection and Estimation.**—Nitrogen is best identified by its failure to respond to any of the tests for other gases. An incombustible gas which does not support combustion, is neutral, and does not react with any ordinary reagent, is probably nitrogen. The best confirmatory test is to pass the gas over heated calcium and identify the calcium nitride produced by its reaction with water to lime and ammonia.

In the same way the proportion of nitrogen in a gas is determined by removing all other gases from the mixture and measuring the residual nitrogen and inert gases. The separation of the latter is a tedious process (Ch. XXV.).

The determination of the proportion of nitrogen in the air is best performed by means of the Hempel burette and pipette. The pipette is charged with sodium pyrogallate solution and is set so that the liquid surface coincides with the mark M. A certain volume of air is enclosed in the burette over mercury, and after levelling the volume is read, the temperature and pressure being noted. The burette and pipette are connected and by opening the tap T and raising the levelling tube, the air is driven over into the bulb of the pipette. After some minutes the process is reversed and the air is drawn back into the burette, leaving the liquid at the same mark M. The volume of residual gas is read off. The process is repeated until no further diminution in volume occurs. If the temperature and pressure alter during the experiment a correction must be made. The sodium pyrogallate absorbs carbon dioxide and oxygen and the residual gas is nitrogen and argon.

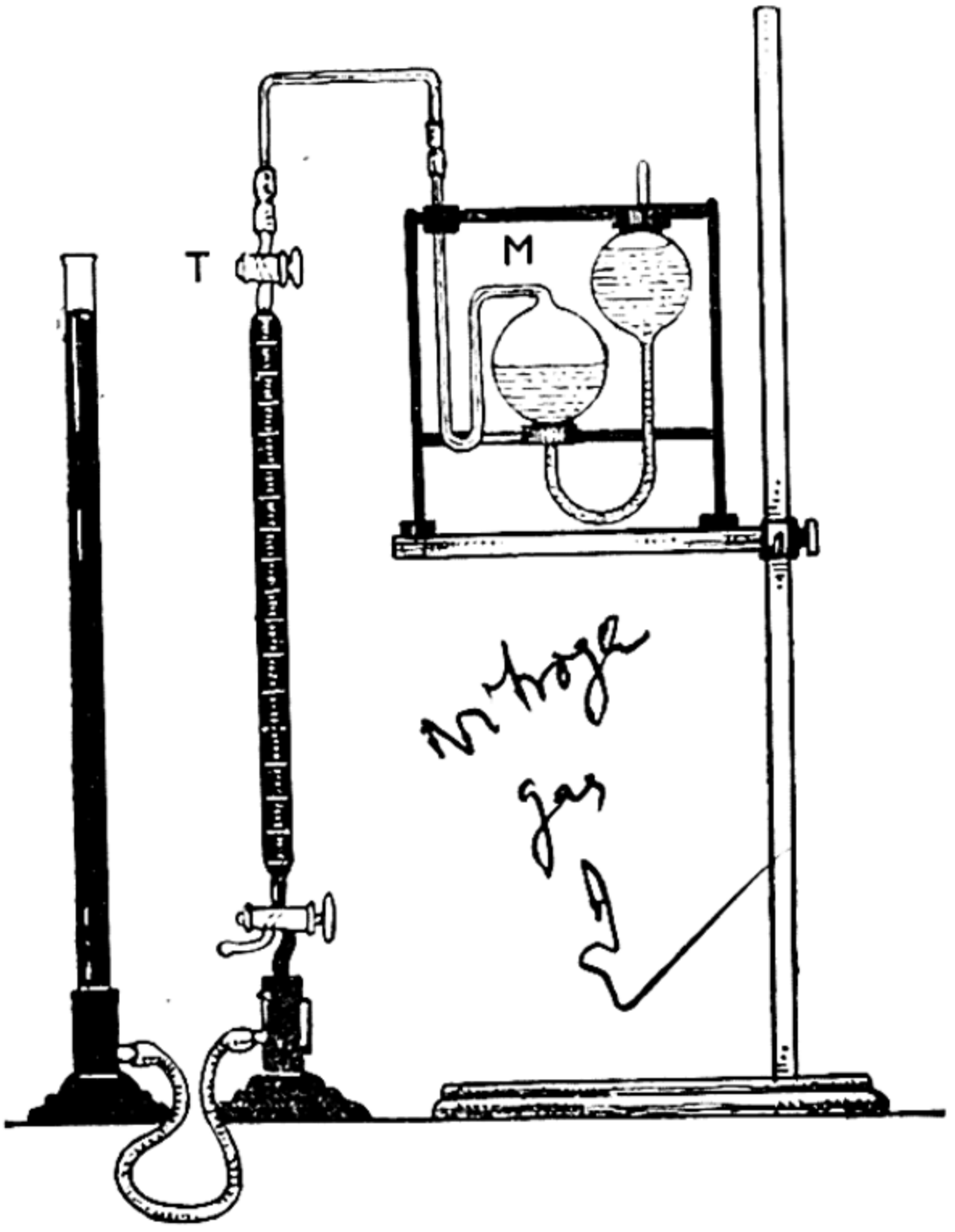


FIG. 129.—Determination of the proportion of nitrogen in air.

The most accurate method is, however, a gravimetric one. The first accurate gravimetric determinations were carried out by Dumas and Boussingault in 1841. They set up an apparatus consisting of an accurately weighed evacuated globe connected to a weighed and evacuated tube containing finely divided copper. This tube was connected to a train of U-tubes containing potash, sulphuric acid, etc. Air was allowed to pass slowly through the U-tubes, which removed carbon dioxide and moisture, and over the strongly-heated

copper which abstracted the oxygen. The nitrogen, with the argon [1] also present, passed into the globe. The difference of the original and final weights of the globe gave the weight of nitrogen, and the difference between the first and last weights of the tube containing the copper gave the weight of oxygen in the same quantity of air. The ratio of these was found to be 76·8 parts nitrogen to 23·2 parts oxygen.

The proportion of nitrogen in a compound is usually determined by the Kjeldahl process, which is applicable to most organic compounds, but not to nitrogen in the form of the nitro-group or nitrates or free nitric acid. The basis of the process is the fact that the nitrogen of most compounds is converted into ammonium sulphate when they are heated with concentrated sulphuric acid and a little mercury. This is determined by the method described on p. 517. Nitrogen in the form of the nitro-group, nitrates or free nitric acid, may be reduced by means of Devarda's alloy (Al, 45%; Cu, 50%; Zn, 5%), and sodium hydroxide, and the resulting ammonia distilled into standard acid.

## Nitrogen Hydrides

There are three hydrides of nitrogen, namely:

| | |
|---|---|
| Ammonia . . . . . | $NH_3$ |
| Hydrazine . . . . . | $N_2H_4$ |
| Hydrazoic acid or Azoimide . . . . | $HN_3$ |

## Ammonia

**686. Historical.**—Ammonia solution was first prepared in the sixteenth century by distilling quicklime, sal ammoniac and water. Priestley isolated the gas by heating the solution and collecting the gas over mercury.

**687. Occurrence.**—Ammonia is a product of the decay of organic compounds containing nitrogen. Thus stable manure, etc., contains the compound urea $CO(NH_2)_2$, derived from the urine of animals. The action of bacteria converts this into ammonium carbonate,

$$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3.$$

This salt decomposes to some extent and produces free ammonia,

$$(NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2,$$

the smell of which is noticeable in stables, etc. Consequently also the air contains traces of the gas.

**688. Preparation.**—Ammonia is prepared, in the laboratory, by the action of alkalis on ammonium salts. On the commercial scale

[1] Not yet discovered in Dumas' time.

it is prepared synthetically from nitrogen and hydrogen or recovered from the "ammoniacal liquor" condensed from crude coal gas §§ 548, 549).

**689. Synthesis of Ammonia from its Elements.**—The gases nitrogen and hydrogen do not react to any appreciable extent under normal laboratory conditions. The reaction between them, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, is exothermic (*i.e.*, gives out heat), and is accompanied by a diminution of volume. It follows then from the laws of van't Hoff and Le Chatelier (§§ 110, 111) that the *yield* of

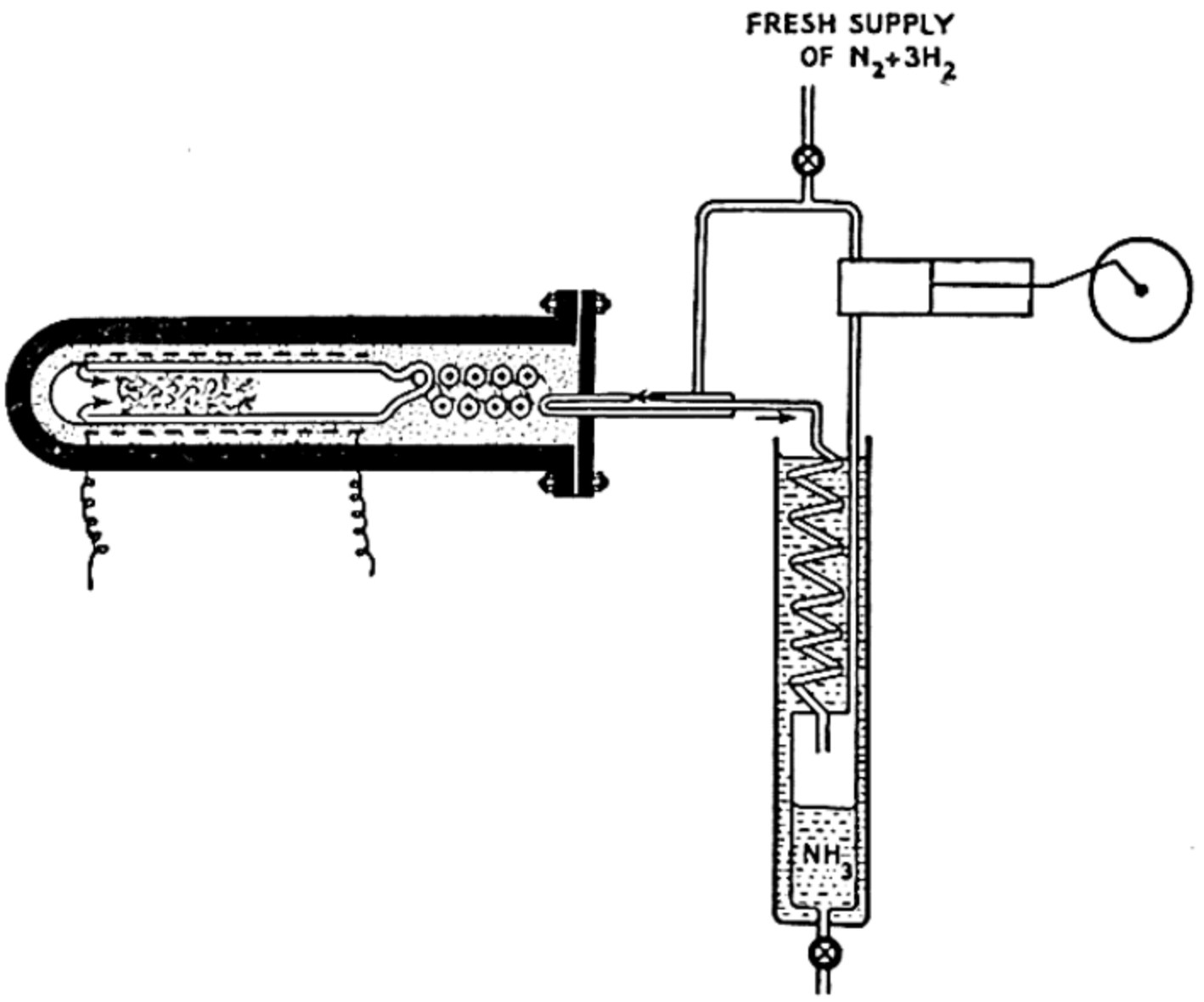


FIG. 130.—Experimental plant used in the synthesis of ammonia.

ammonia is greatest at low temperatures and high pressures. The lowness of the temperature which can be used in practice is limited by the fact that the *speed* of the reaction is diminished by lowering the temperature, though the ultimate *yield*, if time enough be allowed, is improved.

On the commercial scale temperatures of 200°–700° C. have been found suitable, and the speed of the reaction is accelerated by the use of a catalyst usually prepared by melting iron oxide with about one per cent. of its weight of sodium or potassium oxide and about the same small proportion of silica or alumina. The pressures used are limited only by engineering difficulties and the fear of explosion. They vary from 100 to 900 atmospheres, and even the latter enormous figure has been much exceeded in experimental plants.

The hydrogen required is obtained, as a rule, from water-gas (§§ 182 (3), 556), and the nitrogen is obtained by the air-liquefaction process (§ 678) or by combustion of an air-hydrogen mixture. Fig. 130 shows the experimental apparatus originally employed in

the Haber-Bosch process. Nitrogen and hydrogen are compressed to 200–800 atm. and circulated continuously through a very strong steel vessel, in which is an inner vessel containing the catalyst, which may be heated electrically. The issuing gas, containing ammonia, nitrogen and hydrogen, is cooled when liquid ammonia condenses. The remaining nitrogen and hydrogen, together with fresh gas, are again passed over the catalyst. The spiral concentric

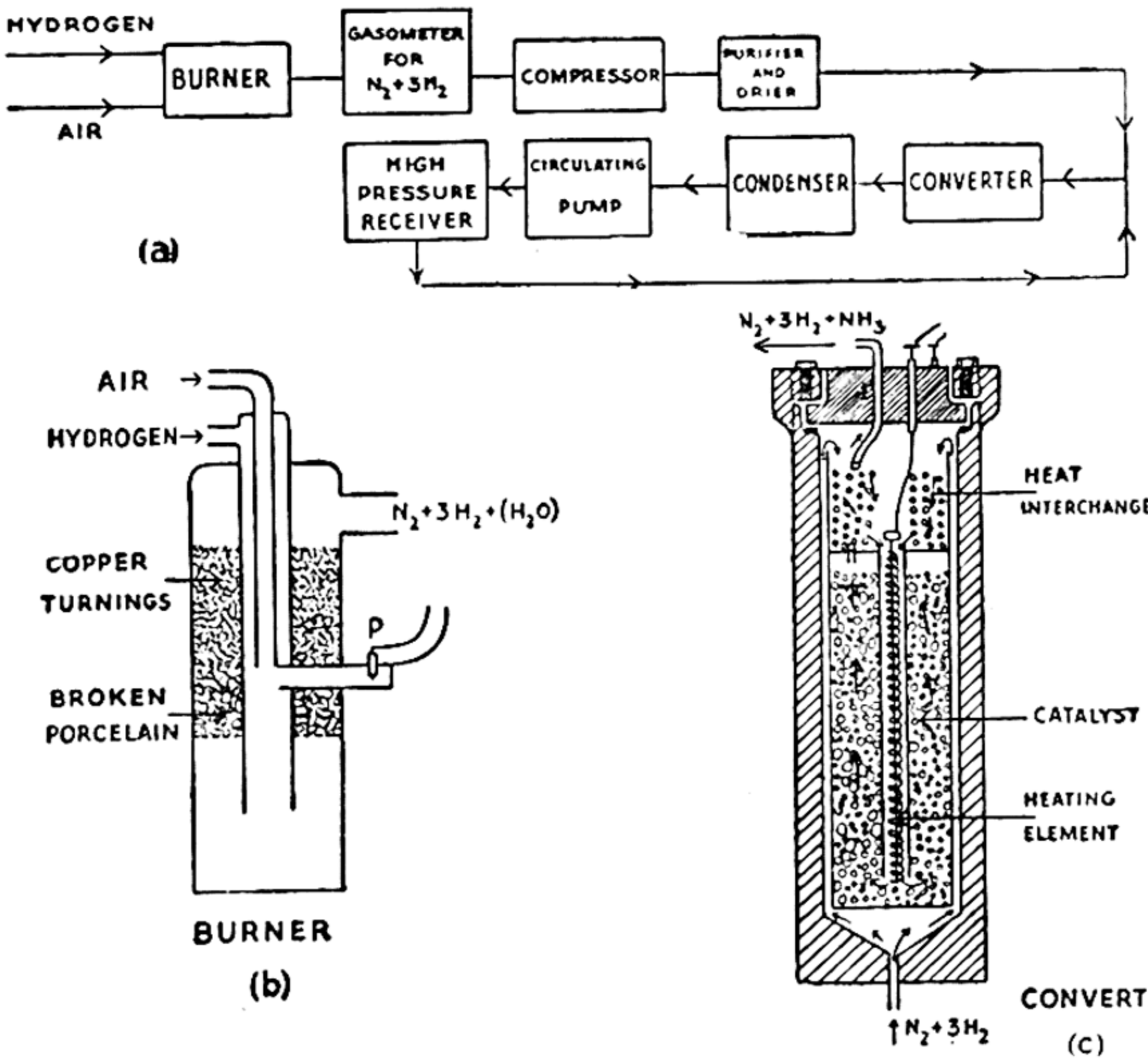


**Fig. 131.—Ammonia Synthesis: (*a*) lay-out of plant; (*b*) burner; (*c*) converter.**

tubes act as a heat interchanger, heating the cold incoming gas and cooling the hot outgoing gas.

On the large scale many modifications have been proposed. A typical plant might be arranged as in Fig. 131 (*a*). The first stage is the preparation of a mixture of nitrogen and hydrogen.

If electrolytic hydrogen is available it is mixed with the appropriate proportion of air in a burner (*b*) and at once ignited by a sparking-plug P. The combustion is completed by passing the gases over broken porcelain and copper turnings heated by the combustion products. The issuing gases contain nitrogen, hydrogen, steam and impurities from the air, and are passed to a gasometer.

Alternatively, water-gas and producer gas may be mixed. The

resulting mixture of nitrogen, carbon monoxide and hydrogen is led together with steam over an iron oxide catalyst, whereupon the reaction $CO + H_2O = CO_2 + H_2$ takes place. The carbon dioxide is removed by washing the compressed gas with water and any residue of carbon monoxide by washing with ammoniacal cuprous formate, leaving a mixture of nitrogen and hydrogen. The gases are then highly compressed, dried and purified. They then pass to the converter (*c*), constructed of alloy steel 3 inches thick. They pass round the outside of the inner shell containing the catalyst, thus helping to keep the outer casing cool. They then pass over the coiled tubes of a heat interchanger and down a central tube containing an electric heating element. Thence they pass up through the catalyst and so to the exterior.

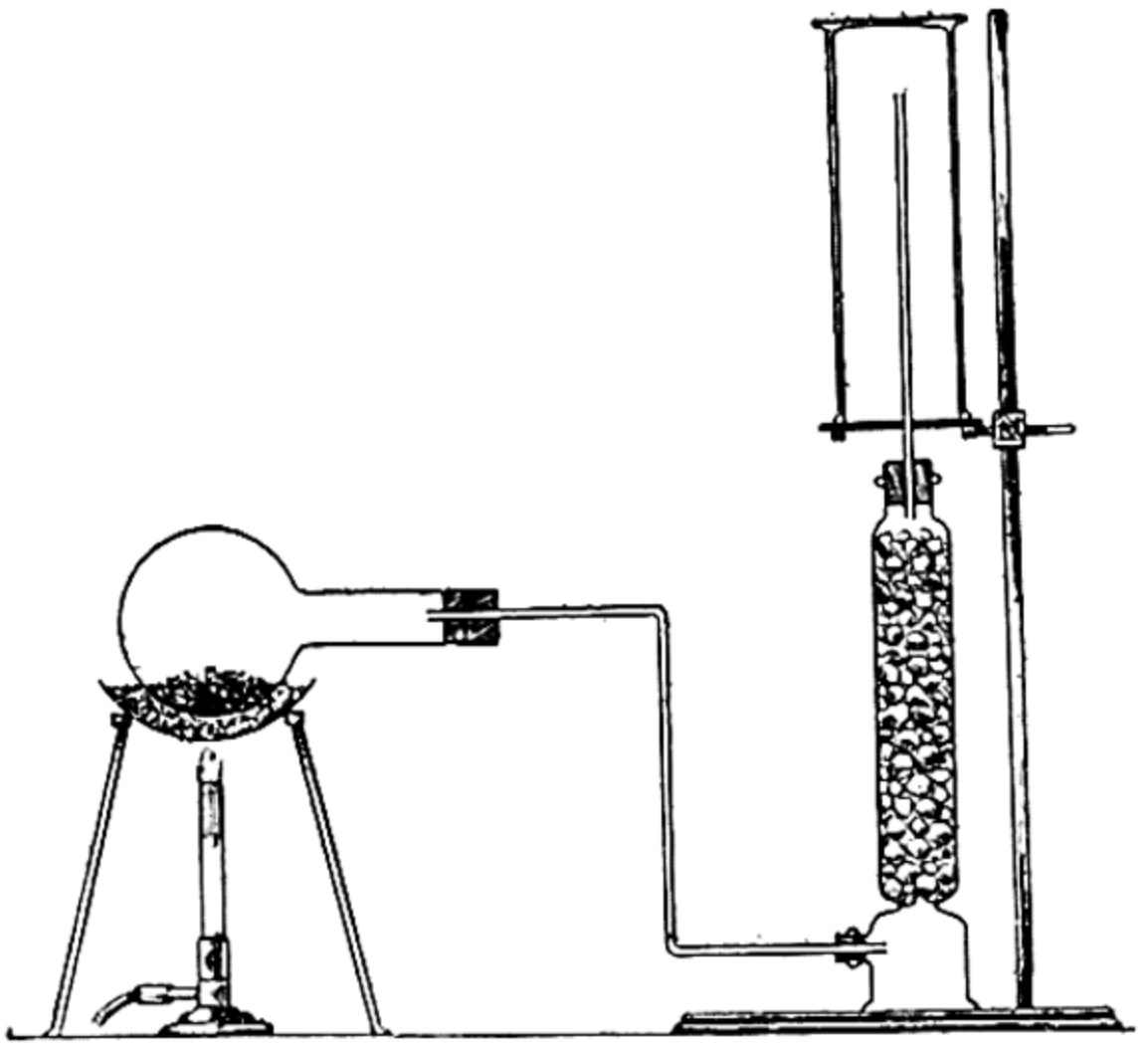

FIG. 132.—Preparation of ammonia.

The ammonia gas at this high pressure may be condensed out merely by passing it through a water-cooled spiral tube.

The unchanged nitrogen and hydrogen are forced by a circulating pump back to the converter.

**690. Ammonia from Coal Products.**—In the process of purifying coal-gas (§§ 548, 549) there are obtained various liquids containing ammonium compounds and ammonia. These liquids contain free ammonia, ammonium carbonate, sulphide, cyanide, sulphate, etc. To obtain ammonia these liquors are heated by means of steam, when the salts of the weaker acids are decomposed and ammonia is carried over,

$$(NH_4)_2CO_3 = 2NH_3 + H_2O + CO_2.$$

The residual liquid is mixed with milk of lime and again heated in a current of steam.

$$Ca(OH)_2 + (NH_4)_2SO_4 = CaSO_4 + 2NH_3 + 2H_2O.$$

Free ammonia is liberated and the mixture of ammonia and steam may be condensed directly to ammonia solution, but is more commonly led into sulphuric acid, thus producing a solution of ammonium sulphate,

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

which is crystallised out. The crystals are dried by means of a centrifuge.

**691. Laboratory Preparation of Ammonia.**—Ammonia is prepared in the laboratory by the action of alkalis, preferably lime, on an ammonium salt, usually the chloride. Powdered quicklime is mixed in a mortar with its own weight of ammonium chloride and transferred to a round flask connected, as shown in Fig. 132, to a tower containing quicklime, and some arrangement for collecting the gas. The gas comes off rapidly when the flask is warmed.

$$CaO + 2NH_4Cl = 2NH_3 + CaCl_2 + H_2O.$$

Ammonia, of course, cannot be collected over water, in which it is very soluble, but being lighter than air it may be collected by displacement as shown in the figure. If the pure gas is required it is necessary to collect it over mercury. Ammonia can only be dried over quicklime or caustic potash or some alkaline drying agent, for it combines with sulphuric acid and phosphorus pentoxide and forms additive compounds with calcium chloride.

There are no other practical methods of preparing ammonia, but the following reactions which lead to its formation are of interest.

The dry distillation of nitrogenous organic matter with or without lime yields ammonia. The distillation of horn was one of the early methods of making ammonia, the solution of which was known as spirits of hartshorn.

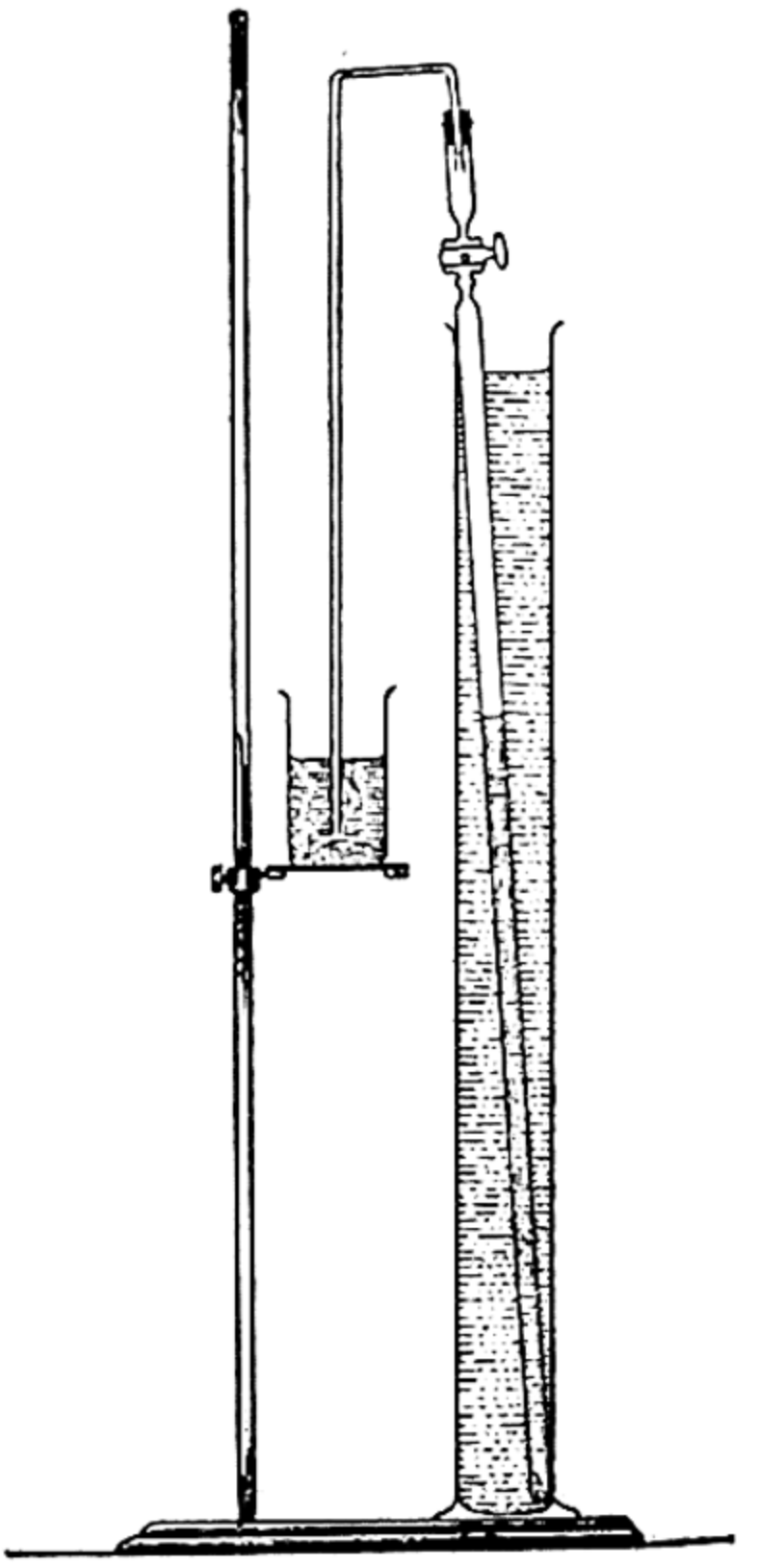

FIG. 133.—Demonstration of composition of ammonia.

The treatment of nitrogenous organic compounds with concentrated sulphuric acid (Kjeldahl process, § 685) converts their nitrogen into ammonium compounds.

The reduction of nitrites, nitrates, etc., with nascent hydrogen also yields ammonia,

$$HNO_3 + 8H = NH_3 + 3H_2O.$$

These salts are often estimated by this process (§ 685).

**692. Structure and Formula.**—Ammonia may be shown to have the formula $NH_3$.

A long glass tube arranged as in Fig. 133 is divided into three equal portions. The tube is filled with chlorine, and in the neck is placed a little concentrated ammonia solution. The tap is cautiously opened and the ammonia solution is admitted a little at a time. The ammonia and chlorine react with a bright flash. When no further reaction occurs the ammonia is emptied from the neck and a little dilute sulphuric acid is introduced to remove the excess of ammonia. The tube is then cooled and opened under water and the volume of nitrogen remaining is one-third of that of the chlorine used. The chlorine present would combine with its own volume of hydrogen and it leaves one-third of its volume of nitrogen. It follows then that one volume of nitrogen and three of hydrogen combine to form ammonia. The formula of ammonia must then contain two atoms of nitrogen for every six of hydrogen, *i.e.*, must be $(NH_3)_n$. Its vapour density is 8·5 at 0° C. and 760 mm. The molecular weight is therefore 17 and $NH_3$ (M. W. $= 14 + 3 \times 1$) is the formula.

The structure of ammonia considered in the light of the electronic theory of valency is

$$\begin{matrix} & & \mathrm{H} & \\ \mathrm{H} & : & \ddot{\mathrm{N}} & : \\ & & \ddot{\mathrm{H}} & \end{matrix}$$

It will be seen that a pair of valency electrons remains available for the formation of co-ordinate linkages, a fact which explains the remarkable tendency of ammonia to form molecular compounds, *e.g.*, $CaCl_2 . 6NH_3$, $Cu(NH_3)_4^{++}$, etc.

We may note the analogous formula of water : $\begin{matrix} & \mathrm{H} & \\ : & \ddot{\mathrm{O}} & : \\ & \ddot{\mathrm{H}} & \end{matrix}$ : which forms similar molecular compounds, hydrates, etc. (§ 208).

**693. Physical Properties.**—Ammonia is a colourless gas with a peculiar alkaline taste and a powerful and characteristic smell. In small quantities it is not poisonous and stimulates the action of the heart, whence its use in smelling salts. In large quantities it rapidly causes death. The saturated solution (·880 ammonia), like most alkalis, is corrosive to the skin. Ammonia gas is lighter than air (D. 8·5). It is readily liquefied by pressure alone. Liquid ammonia boils at — 33·5° C. It has several remarkable properties. It is an excellent solvent, and substances dissolved in it ionise as they do in water. These facts are probably connected with the *association* of liquid ammonia into double and triple molecules and with its donor properties (§ 692).

Liquid ammonia is employed in refrigerating machinery on

account of its volatility and its high latent heat of vaporisation. The usual pattern (Fig. 134) consists of a pump which compresses ammonia and delivers the hot compressed gas to a coil of tubing, where it is cooled and liquefies. The liquid passes into an expansion coil immersed in brine, or a concentrated solution of calcium chloride, which is less corrosive to metal. Here the ammonia evaporates, taking the heat required from the brine. The ammonia is returned to the compressor. The cooled brine may be circulated through refrigerating chambers, etc.

In certain patterns of refrigerator the pump is dispensed with. A vessel containing ammonia dissolved in water under pressure communicates with a second vessel. The ammonia solution is heated

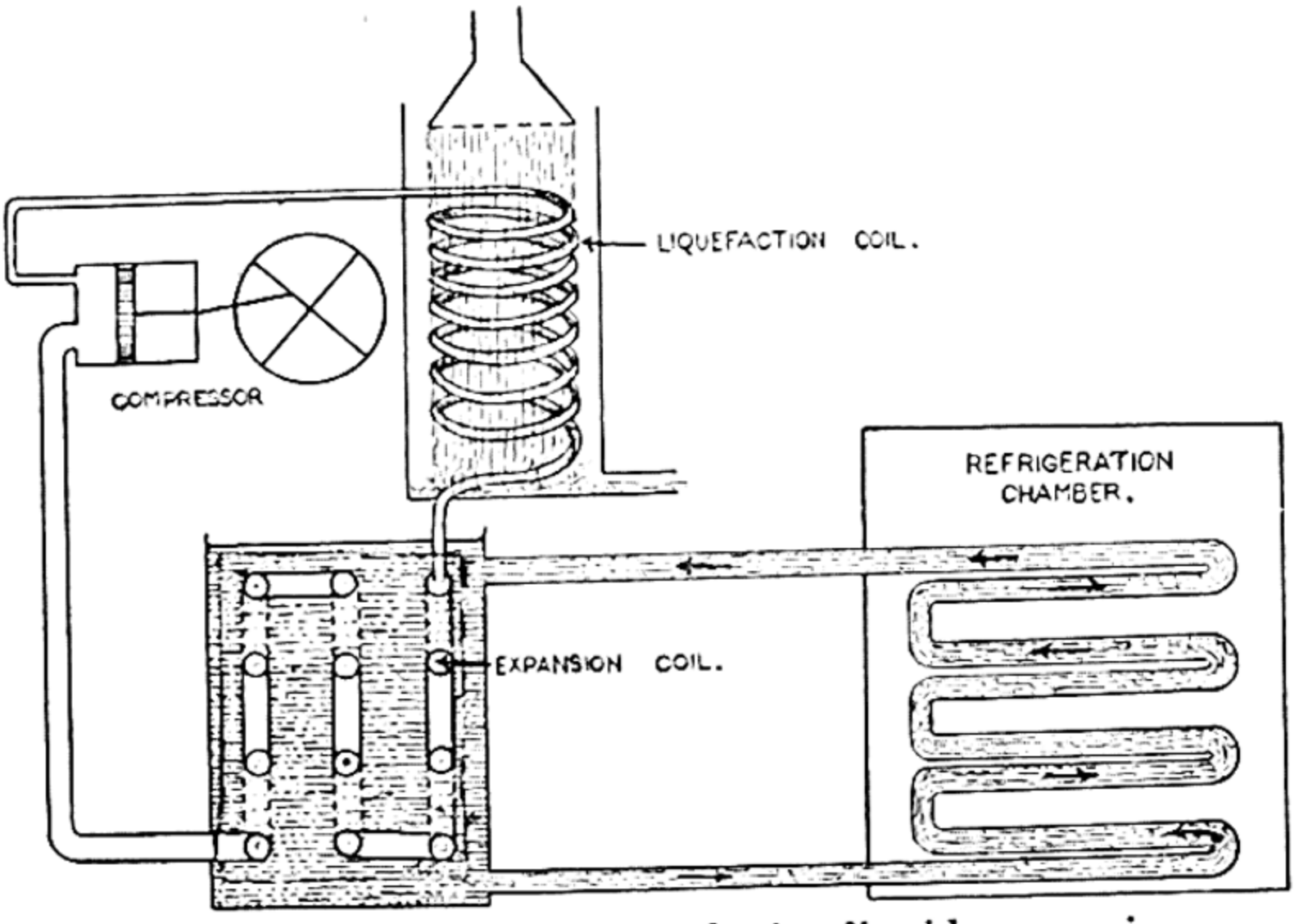


FIG. 134.—Refrigerator employing liquid ammonia.

and the ammonia gas driven into the other vessel liquefies under the influence of the pressure. The heat is then, automatically or otherwise, cut off, the water cools, the liquid ammonia evaporates and the gas formed re-dissolves. The evaporation of the liquid ammonia withdraws the heat from the chamber to be refrigerated.

Ammonia is exceedingly soluble in water, 1 volume of which at 0° C. will dissolve no less than 1,148 volumes of ammonia. This solution contains some 46 per cent. of ammonia by weight. Ammonia is then the most soluble of gases, reckoning the solubility in volumes. The ordinary solution sold as ·880 ammonia is less strong and contains some 35 gms. of ammonia per 100 gms. of solution. Its strength is about 18 N. The solution is further discussed in the next section.

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**694. Chemical Properties.**—Ammonia reacts chemically in three ways :—

(i.) As a hydride and reducing agent.

(ii.) As a base.

(iii.) By forming molecular compounds (ammines).

(i.) *Ammonia as a hydride.*—Ammonia is a comparatively stable gas. It is however decomposed to some extent at a red heat into nitrogen and hydrogen,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3.$$

Ammonia reacts with oxygen, forming water and nitrogen. With air the reaction must be maintained by external heat, but in oxygen ammonia burns with a yellowish flame, while mixtures of oxygen and ammonia explode when ignited,

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

In presence of platinum as a catalyst ammonia may be directly oxidised to oxides of nitrogen, a reaction used in the manufacture of nitric acid (§ 738).

Ammonia reacts with chlorine and bromine, forming nitrogen and the halogen hydride (§ 679). If the halogen

$$3Cl_2 + 8NH_3 = N_2 + 6NH_4Cl$$

is in excess the explosive halides of nitrogen (*q.v.*, § 753) may be formed. Iodine reacts with ammonia, forming a black explosive compound, nitrogen iodide $NH_3 . NI_3$. This substance is distinguished by the extreme ease with which it is exploded, the touch of a feather being enough to detonate it.

Ammonia reacts with the alkali metals, forming amides such as sodamide,

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

The strongest oxidising agents, such as the permanganates, oxidise solutions of ammonia to nitrogen and water.

$$2NH_4OH + 2KMnO_4 = 2KOH + 2MnO_2 + 4H_2O + N_2.$$

The gas is readily oxidised at higher temperatures ; thus when passed over copper oxide, it forms nitrogen and water,

$$2NH_3 + 3CuO = N_2 + 3H_2O + 3Cu.$$

(ii.) *Ammonia as a Base.*—Ammonia not only dissolves in water but also reacts with it ; the process may be represented by the equations,

$$\underset{\text{Ammonia}}{NH_3} + H_2O\ [\rightleftharpoons \underset{\text{Ammonium hydroxide.}}{NH_4OH}] \rightleftharpoons \underset{\text{Ammonium ion.}}{NH_4^+} + \underset{\text{Hydroxyl ion.}}{OH^-}.$$

The presence of free ammonia $NH_3$ is witnessed by its smell and the fact that the gas is evolved from the solution and can be dissolved out of it by solvents, such as chloroform. The presence of ions is shown by the conductivity of the solution, and that of hydroxyl ion $OH^-$ is demonstrated by the alkaline properties. The presence of undissociated $NH_4OH$ ammonium hydroxide is not so certain, and it has been thought that it is not formed and that the true reaction of ammonia with water is

(i.) $$H_2O = H^+ + OH^-.$$

(ii.) $$NH_3 + H^+ = NH_4^+.$$

The weight of the evidence is at present against this last theory. Ammonia solution containing, as it does, the hydroxyl ion behaves as a typical alkali. It has therefore similar properties to those of caustic soda and caustic potash. Ammonia is, however, less dissociated than these and yields a solution containing a smaller proportion of hydroxyl ion ; its alkaline properties are therefore less intense than those of sodium and potassium hydroxides. Ammonia solution reacts with acids to form salts,

$$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O.$$

Ammonia gas also behaves in the same way and, when mixed with hydrogen chloride or other acid gas, forms a dense white smoke, consisting of particles of the ammonium salt of the acid,

$$NH_3 + HCl = NH_4Cl.$$

Ammonia precipitates hydroxides from the salts of many metals (see below). These often dissolve in excess of ammonia, forming complex ions. Thus ammonia, added to a cupric salt, precipitates pale blue cupric hydroxide,

$$2NH_4OH + CuSO_4 = Cu(OH)_2\downarrow + (NH_4)_2SO_4,$$

which dissolves in excess of ammonia, forming the deep blue cuprammonium ion,

$$Cu(OH)_2 \rightleftharpoons Cu^{++} + 2OH^-$$
$$Cu^{++} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{++}.$$

(iii.) *Formation of ammines.*—Ammonia is remarkable for the facility with which it forms molecular compounds, known as ammines. Ammines, which are compounds of the ammonia molecule $NH_3$, must be distinguished from amines and amides, which are compounds of the group $-NH_2$. When the gas is passed over many salts (*e.g.*, $CaCl_2$, $ZnCl_2$) it is absorbed, compounds such as $CaCl_2 . 6NH_3$ being formed. Ammonia also forms additive compounds with many ions, some of which, such as the cobalt-ammines (§§ 1236–8) are very stable.

It is in consequence of the formation of these *complex* ions that ammonia in solution is capable of dissolving many metallic compounds which are insoluble in water. For example, silver chloride is soluble in water only to a minute extent; but the small quantity of silver chloride which dissolves is almost wholly ionised,

$$\underset{\text{Solid.}}{AgCl} \rightleftharpoons Ag^+ + Cl^-.$$

When ammonia is added the silver ion $Ag^+$ is almost completely converted into the argentammonium ion $Ag[NH_3]_2^+$. This reaction removes the silver ion $Ag^+$. In restoring the equilibrium more silver chloride dissolves and ionises and this process continues until the equilibrium

$$Ag^+ + 2NH_3 \rightleftharpoons Ag[NH_3]_2^+$$

is reached. The same argument can be applied to the dissolution of copper hydroxide by ammonia.

These complex ions often form solid salts with acidic ions. Thus the deep blue cuprammonium sulphate, $Cu(NH_3)_4SO_4 . H_2O$, can be precipitated by the action of alcohol from solutions of copper sulphate in ammonia.

The reaction of ammonia solution upon solution of metallic salts may occur in three chief ways :—

(1) The hydroxide may be precipitated as described above. If so, the hydroxide

(*a*) May not dissolve in excess (Al, Fe, Cr, $Sn^{IV}$, Mn, Bi).

(*b*) May dissolve forming a complex ion as described above (Zn, Ni, Co, Cu, Ag).

(2) A hydroxide or basic salt may be formed which dissolves in excess, forming an ammonium salt (As, Sb).

(3) Amines containing the $-NH_2$ group may result,

[Hg (§ 454, 455), Au, Pt.]

**695. Detection and Estimation.**—The gas is readily detected by its smell and by its alkaline reaction. No other gas except methylamine and ethylamine ($CH_3NH_2$, $C_2H_5NH_2$) has an alkaline reaction. A very delicate test is the formation of a yellow precipitate or coloration with Nessler's solution, an alkaline solution of potassium mercuric iodide $K_2HgI_4$ (§ 456). This process is used for the colorimetric estimation of minute traces of ammonia in drinking water, etc.

Ammonia is estimated, like other alkalis, by titration, the best indicator being methyl orange or methyl red. Ammonia in an ammonium salt is best estimated by distilling it with sodium hydroxide and conducting the distillate, ammonia and steam, into a known volume of standard acid. This is titrated after the experiment and the weight of ammonia is estimated as equivalent to the acid used up by the neutralisation of the distillate.

## Ammonium Salts

**696. General Properties.**—In general the ammonium salts are formed by the action of ammonia upon an acid, resemble the salts of the alkali metals. The *ammonium* ion $NH_4^+$, behaves in the combined state very much like the sodium ion $Na^+$, differing chiefly in its behaviour in reactions where strong oxidising agents are present.

Ammonium salts are solids, white or of the colour appropriate to the acid radical. All the commoner salts are soluble in water, only the perchlorate, cobaltinitrite and platinichloride being sparingly soluble. When heated they either decompose or volatilise below a red heat. This property enables them to be separated from the salts of the alkali metals. When they are treated with alkalis ammonia is formed.

**697. Ammonium Chloride.**—Ammonium chloride or *sal ammoniac* has been known since the early middle ages. It was then prepared by subliming a mixture of salt and the soot of burning camel dung. The ammonium carbonate in the soot reacted with the salt, forming the chloride

$$(NH_4)_2CO_3 + 2NaCl = Na_2CO_3 + 2NH_4Cl.$$

The ammonium chloride vaporised and condensed on the lid of the pot used. The name sal ammoniac dates from classical times, but during the first millennium of the Christian era it was applied to other substances, including common salt and possibly 'natron,' native soda, found near the temple of Jupiter Ammon, in Egypt. Ammonium chloride is now made by neutralising the ammoniacal liquor (§§ 547, 548), of the gas-works with hydrochloric acid, evaporating and crystallising the solution. The reaction of ammonium sulphate and sodium chloride is often employed on the large scale. It is frequently purified by sublimation from iron pots on to a concave iron plate.

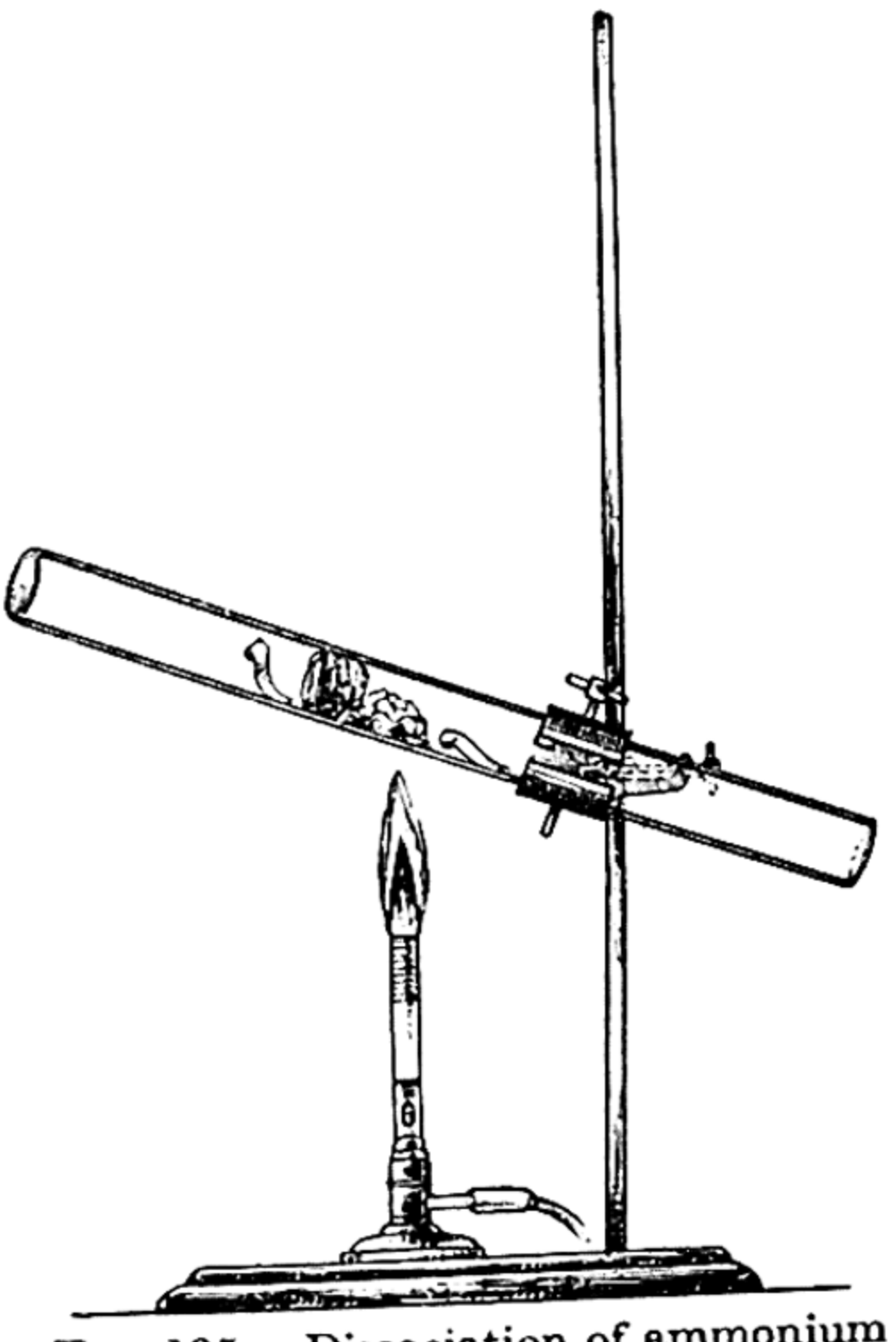


Fig. 135.—Dissociation of ammonium chloride.

The decomposition of ammonium chloride vapour by heat

is of much interest. Ammonium chloride vaporises at about 337° C., and the density of the vapour at 400° C., measured by Victor Meyer's method (§ 52), is found to be only half that corresponding to the formula $NH_4Cl$. This can only be explained by supposing that each molecule of ammonium chloride dissociates into two molecules of, say, ammonia and hydrogen chloride,

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

The vapour, when cooled, forms ammonium chloride once more, but it is possible to separate the ammonia and hydrogen chloride from the hot vapour by diffusion (§ 54), and so demonstrate their presence. The simple apparatus illustrated in Fig. 135 has been used to demonstrate this. An inclined tube has inserted in it a porous plug of asbestos fibre. Below this is placed a little ammonium chloride, and this is heated until it vaporises. The ammonia formed by the dissociation of its vapour diffuses through the plug more rapidly than the denser hydrogen chloride, and pieces of litmus paper placed above and below the asbestos plug are coloured blue and red respectively by the excess of ammonia and of hydrogen chloride. There is still controversy as to whether ammonium chloride, when intensively dried by phosphorus pentoxide, dissociates in this way (*v.* § 205).

Ammonium chloride forms white cubic crystals, resembling those of potassium and sodium chloride. When prepared by sublimation it has a peculiar fibrous structure.

It is soluble in water, 100 gms. of which dissolve 35 gms. of ammonium chloride at 15° C. and 77 gms. at 100° C. In the laboratory it is used as a source of ammonia (§ 691) and more extensively in qualitative and quantitative analysis as a source of the ammonium ion, the latter being required in order to decrease the proportion of hydroxyl ion yielded by ammonia (§ 120).

In industry it has numerous uses. Large quantities are used in the electrolytes of the Leclanché cells, and in the ordinary dry batteries. It is also used as a flux in tin plating, galvanising and soldering.

**698. Ammonium Sulphate** $(NH_4)_2SO_4$ finds considerable use as a fertiliser. It is the usual form in which ammonia is recovered from coal-gas (§ 690), and is also made from synthetic ammonia. In some of the largest works ammonia is converted into ammonium sulphate by means of calcium sulphate (gypsum or anhydrite) which is much cheaper than sulphuric acid. The waste carbon dioxide, produced in obtaining from water-gas the hydrogen needed for synthetic ammonia [§§ 182(3), 556], is passed into ammonia

solution and this is stirred with finely ground calcium sulphate. The reaction

$$2NH_3 + CO_2 + H_2O + CaSO_4 = CaCO_3\downarrow + (NH_4)_2SO_4$$

completes itself in eight or nine hours at 70° C. It is a white crystalline salt, readily soluble in water, 100 gms. of which dissolve 74·2 gms. ammonium sulphate at 15° C., 103·3 gms. at 100° C. It has the usual properties of ammonium salts and sulphates.

**699. Ammonium Nitrate.**—Ammonium nitrate can be made by the action of nitric acid on ammonia,

$$NH_3 + HNO_3 = NH_4NO_3,$$

On the large scale ammonia is oxidised by air in presence of a platinum catalyst (§ 738) to oxides of nitrogen which with water give nitric acid; this is then neutralised with a further quantity of ammonia. Ammonium nitrate forms colourless crystals, which exist in several different crystalline forms. It is very soluble in water, 100 gms. of which dissolve 106 gms. at 15° C. It is of interest on account of its ready decomposition into nitrous oxide and water (§ 707),

$$NH_4NO_3 = N_2O + 2H_2O.$$

It is used on a large scale as an ingredient of explosives and also as a source of nitrous oxide.

A mixture of aluminium powder and ammonium nitrate explodes under the influence of a detonator of lead azide or mercury fulminate. The aluminium burns,

$$2Al + 3NH_4NO_3 = Al_2O_3 + 3N_2 + 6H_2O,$$

and the heat produced decomposes the remaining ammonium nitrate, forming great volumes of nitrogen, oxygen and steam. It is peculiarly safe, for it can neither be ignited by a flame nor detonated by any ordinary shock. The salt finds further uses as a freezing-salt, a low temperature being reached when a large amount of the salt is dissolved in a small quantity of water.

**700. Ammonium Carbonate** was formerly obtained by subliming mixture of ammonium sulphate and chalk, but is now manufactured by passing carbon dioxide and ammonia, both obtained in the synthetic process, together with some steam into leaden chambers where the salt condenses as crusts on the walls.

$$CO_2 + H_2O + NH_3 = (NH_4)HCO_3$$
$$CO_2 + 2NH_3 = NH_4.O.CO.NH_2$$

The product thus actually consists of a mixture of ammonium bicarbonate $NH_4.HCO_3$ with ammonium carbamate $NH_4.O.CO.NH_2$. Carbonic acid has the formula

$CO\langle^{OH}_{OH}$, while carbamic acid is $CO\langle^{NH_2}_{OH}$. Commercial ammonium carbonate forms a white solid which smells strongly of ammonia. The normal carbonate, $(NH_4)_2CO_3$, may be made by treating the solid with strong ammonium hydroxide solution.

**701. Ammonium Sulphides.**—The sulphides of ammonium exist only in solution. Colourless ammonium sulphide contains $(NH_4)_2S$ and $NH_4 . SH$. Yellow ammonium sulphide is a mixture of polysulphides, such as $(NH_4)_2S_n$. When exposed to the air they become oxidised to ammonium thiosulphate and sulphur. Ammonium sulphide finds a considerable use in analysis (§ 804).

**702. Ammonium Phosphates,** $(NH_4)_2HPO_4$, $(NH_4)H_2PO_4$, are commercial products. They find a use in the fire-proofing of fabrics and also in sugar refining.

## Hydrazine $N_2H_4$

**703. Preparation and Properties of Hydrazine.**—This hydride of nitrogen is basic like ammonia, but much less so.

Hydrazine is made by the action of sodium hypochlorite on ammonia in the presence of a small quantity of glue. The glue acts in a manner not clearly understood, but its use prevents the oxidation of the ammonia to nitrogen. Probably chloramine $NH_2Cl$ is first formed,

$$NH_3 + NaOCl = NH_2Cl + NaOH$$
$$NH_2Cl + NH_3 + NaOH = N_2H_4 + NaCl + H_2O.$$

The solution is made acid with sulphuric acid, and the sulphate $N_2H_4 . H_2SO_4$ crystallises out.

Hydrazine salts do not give with alkalis free hydrazine $N_2H_4$, but a stable hydrate $\begin{matrix}NH_2\\|\\NH_3OH\end{matrix}$. From this the pure base is obtained with difficulty by the action of such a powerful alkaline dehydrating agent as barium oxide BaO.

$$BaO + N_2H_6O = Ba(OH)_2 + N_2H_4.$$

The free base is better prepared by the reaction of sodium methylate and hydrazine hydrochloride in solution in dry methyl alcohol,

$$NaOCH_3 + N_2H_4 . HCl = NaCl + CH_3OH + N_2H_4.$$

*Properties.*—Hydrazine is a colourless liquid, which combines with water, giving a weakly alkaline solution of the hydrate. Hydrazine hydrate and hydrazine salts are strong reducing agents, being oxidised to nitrogen. They reduce the salts of the noble metals and of copper to the metal, ferric salts to ferrous salts, etc.

The salts in solution give the ion $N_2H_5^+$.

## Hydrazoic Acid

**704. Preparation and Properties of Hydrazoic Acid, Azoimide, $N_3H$.** The sodium salt of this remarkable compound is made by the action of nitrous oxide on sodamide. Ammonia is passed over heated sodium,

$$2Na + 2NH_3 = 2NaNH_2 + H_2,$$

and nitrous oxide passed over the melted sodamide,

$$NaNH_2 + ON_2 = NaN_3 + H_2O.$$

The latter salt when distilled with 50 per cent. sulphuric acid yields hydrazoic acid.

The formula of the acid is probably $N \leftarrow N = NH$, for the X-ray diagrams of azides show that the three nitrogen atoms lie in a straight line. The ion may be $\left[:\dot{N}:\dot{N}:\dot{N}:\right]^-$ or $\left[N=N\rightarrow N\right]^-$. This agrees well with the method of preparation, for nitrous oxide is probably $:N:::N:\ddot{O}:$ The acid is a highly poisonous volatile liquid boiling at 37° C. It explodes when heated or struck. It is an acid about as strong as acetic acid (dissociation constant *c.* $1{\cdot}8 \times 10^{-5}$). Most of its salts, the azides, are very sensitive explosives, and lead azide $Pb(N_3)_2$ is a more efficient detonator than mercury fulminate (*q.v.* § 447). The azides of the alkali and alkaline earth metals are not explosive but decompose quietly when heated, yielding very pure nitrogen.

## Hydroxylamine

**705. Hydroxylamine $NH_2OH$.**—Hydroxylamine may be made by passing nitric oxide into a solution in which tin is reacting with hydrochloric acid.

$$2NO + 6H = 2NH_2OH.$$

The hydrochloride $HO \cdot NH_3Cl$ is formed.

The best method is by the action of sulphites on nitrites. A concentrated solution of sodium nitrite (2 mols.) is mixed with a solution of sodium carbonate (1 mol.) and sulphur dioxide passed in till just acid. The reaction

$$HO \cdot NO + 2H_2SO_3 = HO \cdot N(SO_3H)_2 + H_2O$$

takes place. The salt $HO \cdot N(SO_3Na)_2$ is formed and the solution is warmed to 90° C. with dilute sulphuric acid, when hydroxylamine sulphate is formed,

$$HO \cdot N(SO_3Na)_2 + 2H_2O = HO \cdot NH_2 \cdot H_2SO_4 + Na_2SO_4.$$

The salt is crystallised out. The free hydroxylamine is made by the action of sodium methoxide on the hydrochloride,

$$HO \cdot NH_3Cl + CH_3ONa = NaCl + CH_3OH + NH_2OH.$$

Hydroxylamine is a white solid and is extremely unstable, decomposing into ammonia and nitrogen,

$$3NH_2OH = NH_3 + N_2 + 3H_2O.$$

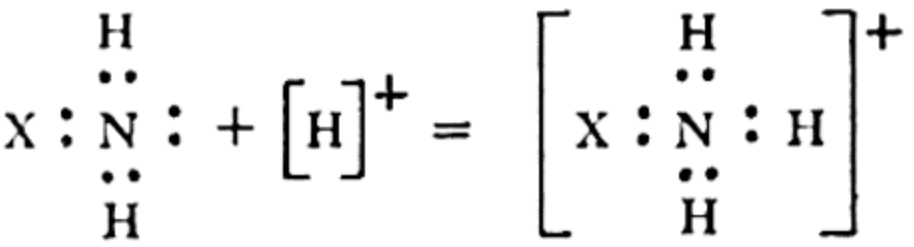
Its salts are fairly stable. They are powerful reducing agents, converting the salts of the noble metals into free metal and cupric salts into cuprous oxide. Oxides of nitrogen or free nitrogen are the products.

On the other hand, hydroxylamine salts oxidise ferrous salts to ferric salts, ammonia being formed.

It should be noted that hydroxylamine, hydrazine, ammonia, and, in general, all basic compounds where salts are formed by attachment of the acid radical to nitrogen, form salts by *addition* of the whole acid molecule, not by *replacement* of the acid hydrogen. In each case we have

$$X-N\begin{matrix}H\\ \\H\end{matrix} + HA = \left[X-N\begin{matrix}H\\H\\H\end{matrix}\right]^+ A^-$$

or, represented according to the electronic theory of valency,



This behaviour of the $-NH_2$ or amino group is of peculiar interest on account of the commonness of amino-compounds in organic chemistry. These salts are often known as "hydrochlorides," etc. Thus we speak of $HO.NH_3Cl$ as hydroxylamine hydrochloride rather than as hydroxylammonium chloride, and of $CH_3NH_3Cl$. as methylamine hydrochloride rather than methylammonium chloride. None the less, these are all true chlorides, and furnish the chloride ion in solution,

$$CH_3NH_3Cl \rightleftharpoons [CH_3.NH_3]^+ + Cl^-.$$

## THE OXIDES AND OXYACIDS OF NITROGEN.

**706. Oxides and Oxyacids of Nitrogen.**—These compounds are for the most part of great industrial importance. The demand for nitrates as fertilisers and for nitric acid in so many important industries, such as the manufacture of explosives, dyes and drugs, has led to the development of methods of manufacture based on the formation of oxides of nitrogen from the air and the subsequent conversion of these to nitrates. There are six oxides of nitrogen :—

| | |
|---|---|
| Nitrous oxide . . . . | $N_2O$ |
| Nitric oxide . . . . | $NO$ |
| Dinitrogen trioxide . . . | $N_2O_3$ $(N_4O_6)$ |
| Nitrogen tetroxide (peroxide) . | $NO_2 \rightleftharpoons N_2O_4$ |
| Nitrogen pentoxide . . . | $N_2O_5$ |
| Nitrogen trioxide . . . | $NO_3$ |

The oxyacids of nitrogen include :—

| | |
|---|---|
| Hyponitrous acid . . . | $H_2N_2O_2$ |
| Hydronitrous acid . . . | $H_2NO_2$ |
| Nitrous acid . . . . | $HNO_2$ |
| Nitric acid . . . . | $HNO_3$ |
| (Pernitric acid . . . . | $HNO_5$) |

### NITROUS OXIDE

**707. Preparation.**—The gas was discovered by Priestley, who acted on nitric oxide (nitrous air) with moist iron filings. He obtained a gas, 'diminished nitrous air,' which had properties different from nitric oxide,

$$2NO + Fe + H_2O = N_2O + Fe(OH)_2.$$

Davy investigated its properties in 1799.

Nitrous oxide is best prepared—

(1) By the action of heat on ammonium nitrate.

(2) By the action of stannous chloride on nitric acid.

The preparation of the gas by reduction of nitrites and nitrates may be carried out in several ways, but the above (2) is the simplest.

(1) It is necessary to take care that ammonium nitrate be not heated too strongly, particularly if it is not pure. Violent and even explosive evolution of gas may occur if the temperature rises too high,

$$NH_4NO_3 = N_2O + 2H_2O.$$

Thirty grams of ammonium nitrate are placed in a 500 c.c. round-bottomed flask fitted with safety tube, thermometer and delivery tube, and wash-bottles as described below. The flask is steadily heated to 255° C., care being taken that the evolution of gas is not too rapid. A mixture of ammonium sulphate and sodium nitrate may be used and gives a slower current of gas (cf. § 679 (1) ). The gas should be collected over mercury or over hot water, for its solubility in cold water is inconveniently great.

The gas as it leaves the flask contains much moisture and some nitric oxide and traces of chlorine arising from ammonium chloride present in the nitrate as an impurity.

These are removed by washing with ferrous sulphate and caustic soda solutions and drying with sulphuric acid. The last process is, of course, omitted if the gas is to be collected over water.

(2) A solution containing 5 parts of stannous chloride, 10 parts hydrochloric acid (sp. gr. 1·21), and 0·9 part nitric acid (sp. gr. 1·38), when heated to boiling evolves a stream of nitrous oxide, which should be washed and dried as above,

$$2HNO_3 + 4SnCl_2 + 8HCl = 4SnCl_4 + 5H_2O + N_2O.$$

**708. Formula.**—The decomposition of nitrous oxide by heated copper shows that 1 volume of the gas yields 1 volume of nitrogen. The formula is therefore $N_2O_n$. Since the vapour density is 22 ($H_2 = 1$), the molecular weight is 44 and the formula $N_2O$, ($2 \times 14 + 16$). Its structure is linear and is probably $N \equiv N \rightarrow O$.

**709. Physical Properties.**—Nitrous oxide, sometimes called 'laughing gas,' is a colourless gas which has a sweetish taste and pleasant odour. The smell of the gas as given by the dentist is is largely due to the rubber bag from which it usually is administered.

Nitrous oxide is not poisonous and, when mixed with enough oxygen to enable it to support life, may be inhaled for hours. In

small quantities it is said to produce exhilaration, and Davy, after inhaling it, capered and danced round the laboratory 'like a madman.'

The gas probably affects the highest mental functions [1] first, and, like alcohol, causes a man to lose control of his behaviour and follow his instincts. Davy laughed and capered because he was exhilarated by making a scientific discovery; dental patients often hit the dentist, but do not commonly laugh.

In larger quantities nitrous oxide produces anæsthesia of a safe but not very deep type. It is chiefly used for dental operations, but finds considerable use in surgery, and is often used to induce anæsthesia, which is then maintained by ether or chloroform.

Nitrous oxide liquefies when cooled to a liquid boiling at — 88° C. Its critical temperature is *c.* 36° C., and it can therefore be liquefied by pressure alone. The liquid solidifies at — 102° C. The gas is moderately soluble in water. At 15° C. water dissolves about three quarters of its volume of the gas.

Nitrous oxide is readily decomposed by heat into its components,

$$2N_2O = 2N_2 + O_2,$$

at a red heat and above.

It therefore readily supports combustion, for almost any burning substance is hot enough to decompose the gas and so form a mixture of two parts of nitrogen and one part of oxygen, which supports combustion more vigorously than air. Feebly burning sulphur or a splinter just tipped by a feeble spark do not produce enough heat to do this and are extinguished in the gas.

Like all oxides of nitrogen it is decomposed when passed over red-hot copper,

$$N_2O + Cu = CuO + N_2.$$

It behaves as a neutral oxide. Its formula is that of the anhydride of hyponitrous acid $H_2N_2O_2$, but shows none of the properties of an acidic oxide.

**710. Detection.**—Nitrous oxide may be distinguished from oxygen by the fact that it is not absorbed by sodium pyrogallate solution, and does not give brown nitrogen tetroxide when mixed with nitric oxide. From other neutral gases it is distinguished by

[1] "Nitrous oxide . . . when sufficiently diluted with air stimulates the mystical consciousness in an extraordinary degree. Depth beyond depth of truth seems revealed to the inhaler. This truth fades out, however, or escapes, at the moment of coming to; and if any words remain over in which it seemed to clothe itself, they prove to be the veriest nonsense. Nevertheless, the sense of a profound meaning having been there persists; and I know more than one person who is persuaded that in the nitrous oxide trance we have a genuine metaphysical revelation."—William James: "The Varieties of Religious Experience."

the fact that it relights a brightly glowing splinter of wood. If other nitrogen oxides are contained in the gas mixture these should be removed by absorption with ferrous sulphate solution.

## Nitric Oxide

**711. Historical.**—Nitric oxide was apparently observed by van Helmont and later by Mayow in 1674, but was first investigated by Priestley in 1772. In each case the gas was prepared by the action of metals on nitric acid.

**712. Preparation.**—(1) Nitric oxide is formed when mixtures of nitrogen and oxygen, *e.g.*, air, are exposed to very high temperatures,

$$N_2 + O_2 \rightleftharpoons 2NO.$$

The reaction is fully discussed under synthetic nitric acid (§ 737).

(2) Nitric acid reacts with most metals (§ 744), and the normal product of the action of the moderately diluted acid upon metals is nitric oxide. The best method of preparation is to allow nitric acid (sp. gr. 1·2[1]) to act on copper turnings. The gas contains a certain amount of nitrogen tetroxide. It may be somewhat purified by passing through water or by absorption in ferrous sulphate solution, from which it is again liberated by the action of heat.

(3) A pure gas is obtained by pouring concentrated sulphuric acid into a solution of ferrous sulphate and potassium nitrate in such a manner that the acid forms a lower layer covered by the solution.

$$2KNO_3 + 6FeSO_4 + 4H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + 2NO + 4H_2O.$$

(4) A very pure gas is prepared by dropping 50 per cent. sulphuric acid into a concentrated solution of sodium nitrite (2 parts) and potassium iodide (1 part); the resulting nitrous and hydriodic acids react giving nitric oxide and iodine.

$$2HNO_2 + 2HI = 2NO + I_2 + 2H_2O.$$

The gas may also be prepared by numerous other methods based on the reduction of nitrites and nitrates.

**713. Formula.**—The gas may be decomposed by a heated nickel spiral (§ 684), when it is found that (*a*) the gas is halved in volume while (*b*) the nickel increases in weight by 53·33 per cent. of the weight of the gas,

$$2Ni + 2NO = 2NiO + N_2.$$

The first piece of evidence (*a*) shows that one molecule of nitrogen ($N_2$) forms two molecules of nitric oxide, and that consequently the formula is $NO_n$. The percentage of oxygen in this must be $\frac{100 \times 16n}{14 + 16n}$,

[1] Equal parts of water and 'concentrated' nitric acid (sp. gr. 1·4).

and since this is equal to 53·33 (*b*), *n* must be 1 and the formula is NO. This formula cannot be reconciled with the usual valency relationships of oxygen and nitrogen, and may be written N = O. We may write this $\dot{\ddot{O}}\vdots\dot{N}\cdot$ or perhaps $\ddot{O}\vdots N:$

Nitric oxide is one of the few compounds with an odd number of valency electrons. Its reactivity is in favour of this formula. It is hard to understand why the double molecule, $N_2O_2$, O=N−N=O, is not formed.

**714. Physical Properties.**—Nitric oxide is a colourless gas, the smell and taste of which cannot be ascertained, since it reacts with air and forms the pungent nitrogen tetroxide. The gas is heavier than air [D. 15 ($H_2 = 1$), 1·038 (air = 1)]. It is liquefied and solidified only at very low temperatures, the melting point being — 160·6° C., and the boiling point — 150·2° C.

It is sparingly soluble in water, which dissolves about one-twentieth of its volume of the gas at 15° C. It dissolves freely in solutions of ferrous salts, with which it combines chemically. Loose compounds of dark colour, such as $FeSO_4.NO$, $FeCl_2.NO$, are formed, some of which have been isolated. Solutions of copper sulphate, and of nickel, cobalt, and manganese salts, also dissolve the gas, probably forming similar compounds.

**715. Chemical Properties.**—Nitric oxide is decomposed only at high temperatures. The reaction is

$$N_2 + O_2 \rightleftharpoons 2NO - 43{\cdot}15 \text{ Cals.}$$

It therefore follows that a rise of temperature tends to increase the proportion of nitric oxide present in the *equilibrium mixture*. At lower temperatures, below 500° C., the reaction is so slow that equilibrium is not reached and the gas appears stable. Round about 1,500° C. the gas decomposes almost completely, equilibrium being rapidly attained. At higher temperatures, up to 3,000° C., the equilibrium shifts to the right, and a fair proportion of the gas (up to 5 or 6 per cent.) persists at equilibrium.

Most combustibles are extinguished by the gas, but strongly burning phosphorus or charcoal decomposes the gas and burns brilliantly in the oxygen so produced.

Many metals are oxidised when heated in the gas,

$$2Cu + 2NO = 2CuO + N_2.$$

The gas can be reduced and also oxidised.

Oxidising agents convert the gas into nitrogen peroxide or nitric acid. The gas is particularly notable as combining directly with oxygen in the cold, forming the brown gas, nitrogen tetroxide,

$$2NO + O_2 = 2NO_2.$$

If the reaction takes place over water the latter gas is absorbed. The earliest method of determining the proportion of oxygen in a gas was to collect it in a graduated vessel over water or caustic potash, and bubble in nitric oxide as long as any brown colour was produced. The diminution in volume indicated the proportion of oxygen present. Other oxidising agents mostly produce nitric acid. Thus, with iodine in dilute solution nitric acid and hydrogen iodide are produced,

$$3I_2 + 4H_2O + 2NO = 2HNO_3 + 6HI.$$

With potassium permanganate, nitric acid is formed,

$$10NO + 6KMnO_4 + 12H_2SO_4 = 10HNO_3 + 6KHSO_4 + 6MnSO_4 + 4H_2O.$$

Nitric oxide reacts with certain reducing agents. Thus the metals (*v. supra*) reduce it to nitrogen, and when it is exploded with hydrogen the same result occurs,

$$2NO + 2H_2 = 2H_2O + N_2.$$

If, however, the gas mixed with hydrogen is passed over platinum black or certain other metallic catalysts it is reduced to ammonia,

$$2NO + 5H_2 = 2NH_3 + 2H_2O.$$

Some reducing agents, such as sulphurous acid, reduce it to nitrous oxide,

$$2NO + H_2SO_3 = N_2O + H_2SO_4,$$

while stannous chloride reduces it to hydroxylamine (*q.v.*).

Concentrated aqueous potassium hydroxide decomposes the gas, forming nitrites and nitrous oxide,

$$4NO + 2KOH = N_2O + 2KNO_2 + H_2O.$$

The addition products of nitric oxide and metallic salts have been alluded to above (§ 714). With chlorine and bromine it combines additively, forming nitrosyl chloride and nitrosyl bromide,

$$2NO + Cl_2 = 2NOCl.$$

**716. Detection.**—The production of a brown colour when a colourless gas is mixed with air is evidence of the presence of nitric oxide. If nitrogen peroxide is also present, difficulty is caused by the reaction of the two gases to form the acidic trioxide which reacts with water giving nitrous acid. For this reason,

$$NO_2 + NO \rightleftharpoons N_2O_3$$
$$N_2O_3 + H_2O = 2HNO_2$$

nitric oxide cannot, unless it is in large excess, be separated from nitrogen peroxide by absorption of the latter with water or potash.

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## Dinitrogen Trioxide.

**717. Preparation.**—This unstable compound is prepared by mixing nitric oxide and nitrogen peroxide,

$$NO_2 + NO \rightleftharpoons N_2O_3.$$

On cooling the mixture to − 30° C. the trioxide condenses as a blue liquid.

It may also be prepared by the action of nitric acid on arsenic trioxide,

$$As_2O_3 + 2HNO_3 = N_2O_3 + 2HAsO_3.$$

Acid of sp. gr. 1·5 should be used, cooling often being necessary to moderate the reaction. The gases are dried over calcium chloride and condensed in a ∪-tube cooled in ice and salt.

The action of nitric acid, five to six times normal (sp. gr. 1·17), on copper yields the trioxide,

$$6HNO_3 + 2Cu = 2Cu(NO_3)_2 + 3H_2O + N_2O_3.$$

In both the last cases very little of the actual trioxide is formed, the gas being mainly a mixture of nitrogen tetroxide and nitric oxide, which react on cooling to form the liquid trioxide.

**718. Physical Properties.**—Dinitrogen trioxide is at room temperatures about 97 per cent. dissociated into nitrogen peroxide and nitric oxide. It behaves therefore, physically and chemically, like a mixture of these gases. The liquid boils at − 2° C.[1] and it is not dissociated below − 21° C.

The gas at ordinary temperatures contains the molecules $N_2O_3$, $N_4O_6$, NO, $NO_2$ and $N_2O_4$.

The gas in most respects behaves as a mixture of these gases. Thus the gas reacts with water, forming both nitrous and nitric acids, free nitric oxide remaining undissolved. It is, however, absorbed by dry potash, forming only potassium nitrite,

$$N_2O_3 + 2KOH = 2KNO_2 + H_2O.$$

## Nitrogen Tetroxide.

**719. History.**—Nitrogen tetroxide in the form of 'brown fumes' was noticed by Hales, Priestley and Scheele. Its formula was first accurately determined by Gay-Lussac in 1816.

**720. Preparation.**—(1) Nitrogen tetroxide may be made by mixing nitric oxide and oxygen in the proportions indicated in the equation

$$2NO + O_2 = N_2O_4.$$

The method is not a convenient one in practice.

(2) The decomposition of the nitrate of any one of the heavy metals by heat produces the gas mixed with some oxygen. Lead nitrate is best, for since it is anhydrous, the gas from it is dry,

$$2Pb(NO_3)_2 = 2PbO + 2N_2O_4 + O_2.$$

(3) The action of nitric acid on sodium nitrite yields the gas,

$$NaNO_2 + 2HNO_3 = NaNO_3 + H_2O + N_2O_4.$$

[1] Widely varying figures, − 27° C. to 43° C., are given. The differences depend perhaps, on the degrees of purity and dryness of the material.

In each case the gas may be collected by downward displacement, or, better, dried with phosphorus pentoxide and condensed in a U-tube surrounded by ice and salt. It forms a yellow liquid, which may be vaporised once more, giving the pure gas.

**721. Physical Properties.**—Nitrogen tetroxide is a brown gas which deepens in colour when heated owing to dissociation (*v.* below). It has a pungent smell and acid taste and is very poisonous. When cooled it condenses to a yellow liquid, boiling at 22° C., and it freezes to a colourless solid melting at — 11° C.

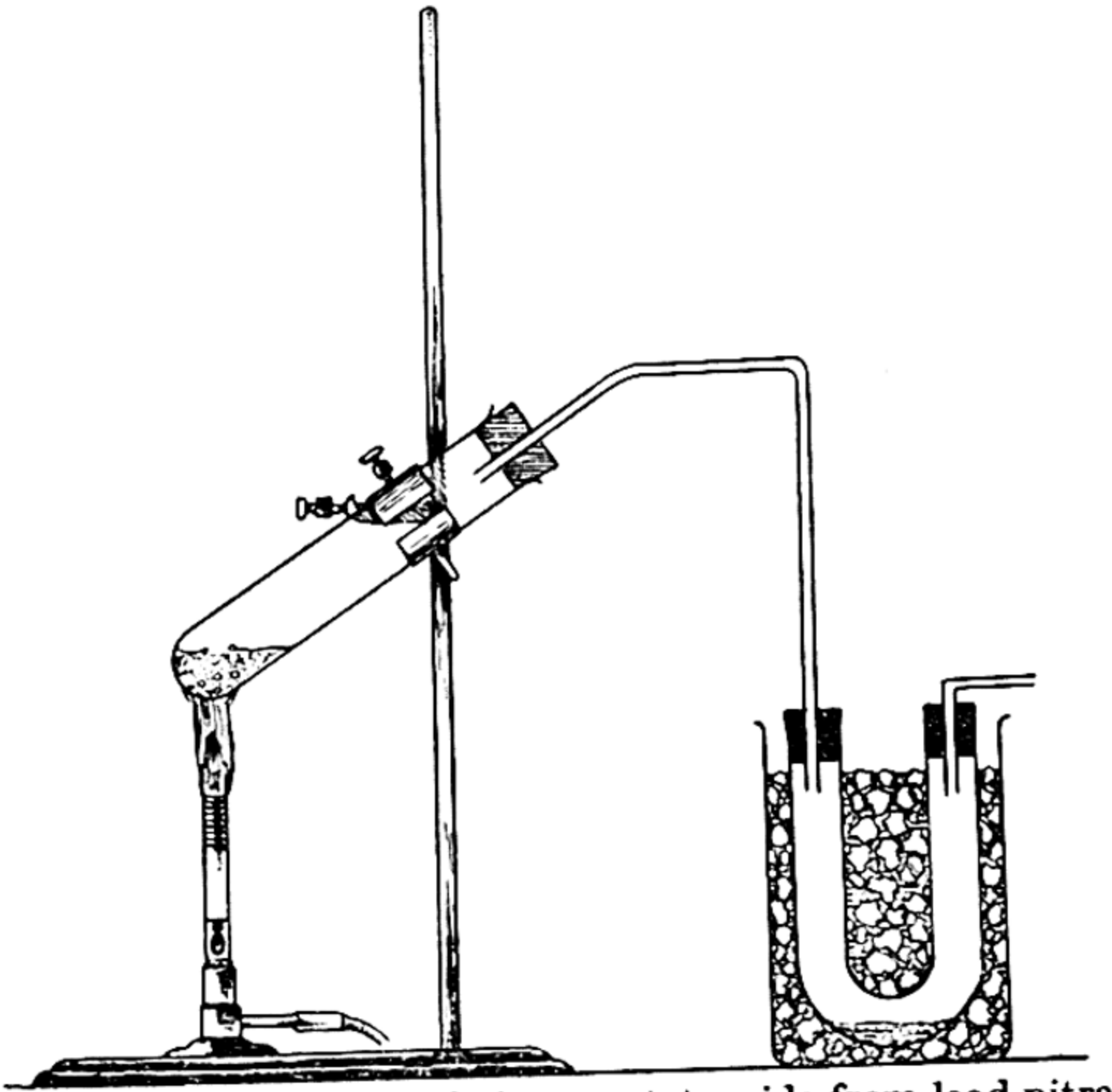


FIG. 136.—Preparation of nitrogen tetroxide from lead nitrate.

The density of the gas does not correspond to the value for the formula $NO_2$ or $N_2O_4$, but is intermediate between the two values.

| Temperature. | Observed Density of Gas referred to Hydrogen at the same Temperature. | Per cent. $NO_2$ by Volume (calculated). |
|---|---|---|
| 26·7 | 38·15 | 34·0 |
| 39·8 | 35·4 | 46·0 |
| 60·2 | 29·9 | 69·8 |
| 80·6 | 25·9 | 87·7 |
| 100·1 | 24·2 | 94·8 |
| 121·5 | 23·3 | 98·6 |
| 135·0 | 23·05 | 98·8 |

The densities of nitrogen peroxide at various temperatures have been determined, and from them we deduce that nitrogen tetroxide contains both molecules, $NO_2$ and $N_2O_4$, in equilibrium.

The calculation of the percentages of $NO_2$ and $N_2O_4$ by volume may be performed as follows :—

Let 11·2 litres of the gas contain $x$ litres of $NO_2$ and $(11{\cdot}2 - x)$ litres of $N_2O_4$.

The weight of 11·2 litres of the gas is the density referred to hydrogen.

The weight of the $NO_2$ and $N_2O_4$ is their volume in litres multiplied by their molecular weight and divided by 22·4.

$$\therefore \qquad \text{V.D.} = \frac{x \,.\, 46}{22{\cdot}4} + \frac{(11{\cdot}2 - x)92}{22{\cdot}4}.$$

$$\text{V.D.} = 46\frac{(22{\cdot}4 - x)}{22{\cdot}4}.$$

If we term the *percentage* of $NO_2$ $p$, $x = \frac{11{\cdot}2\,p}{100}$,

and we have

$$\text{V.D.} = \frac{46\ (22{\cdot}4 - {\cdot}112\,p)}{22{\cdot}4}.$$

$$\text{V.D.} = 46\ (1 - {\cdot}005\,p).$$

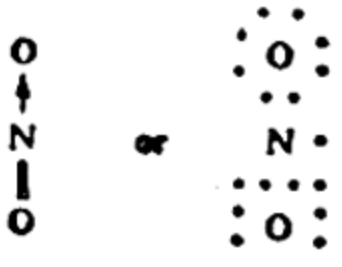
and

$$p = 200\ (1 - \frac{\text{V.D}}{46}).$$

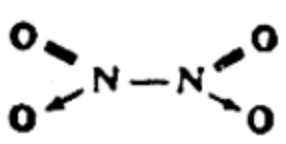
**722. Structure and Formula.**—The considerations of its density (above) and the decomposition of the gas by copper or nickel (cf. § 713) show that the gas is an equilibrium mixture,

$$2NO_2 \rightleftharpoons N_2O_4.$$

$NO_2$ is probably




While $N_2O_4$ is




The nitrogen atom in $NO_2$ has only a septet of electrons and is ready to complete its octet by forming addition products.

**723. Chemical Properties.**—Nitrogen tetroxide does not burn, nor does it support the combustion of feebly burning substances. Substances such as phosphorus and glowing charcoal, which produce a high temperature when they burn, decompose the gas and burn in the oxygen produced,

$$2NO_2 + 2C = 2CO_2 + N_2.$$

Some substances are oxidised when heated in the gas and reduce it only to nitric oxide. Thus carbon monoxide burns in the gas, forming carbon dioxide and nitric oxide,

$$CO + NO_2 = CO_2 + NO.$$

Sodium and some other metals behave similarly,

$$Pb + NO_2 = PbO + NO.$$

Nitrogen tetroxide is absorbed by certain metals, forming 'nitro-metals,' which are sometimes regarded as compounds, but are more probably the result of adsorption.

Certain salts form loose compounds with nitrogen tetroxide, such as $4FeCl_2.NO_2$, much resembling the compounds formed with nitric oxide, such as $FeSO_4.NO$.

The reaction of nitrogen tetroxide and water is of importance from the point of view of the nitric acid industry (§ 738).

Nitrogen tetroxide reacts with water, first of all forming nitric and nitrous acids,

$$N_2O_4 + H_2O = HNO_2 + HNO_3.$$

Unless the liquid is ice-cold, some or all of the nitrous acid then decomposes. If but little water is present, nitrogen trioxide and water result,

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O,$$

but in presence of much water nitric acid and nitric oxide are formed,

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

In presence of excess of air this nitric oxide is converted into nitrogen tetroxide, which reacts with more water as already described; so that in presence of excess of oxygen and water at a temperature high enough to decompose nitrous acid, nitric acid would be the sole product

$$2H_2O + 2N_2O_4 + O_2 = 4HNO_3.$$

The reaction is of importance in the synthesis of nitric acid (p. 539).

Nitrogen tetroxide is absorbed by alkalis, nitrates and nitrites being formed, together with a little nitric oxide according to the equations

(1)
$$N_2O_4 + H_2O = HNO_2 + HNO_3$$
$$HNO_3 + HNO_2 + 2KOH = KNO_3 + KNO_2 + 2H_2O$$

(2)
$$\left[\begin{array}{l} 3HNO_2 = HNO_3 + 2NO + H_2O \\ HNO_3 + KOH = KNO_3 + H_2O \end{array}\right].$$

On account of this formation of nitric oxide caustic alkalis are not very perfect absorbents for nitrogen tetroxide. Nitrogen tetroxide is soluble in concentrated sulphuric acid, forming nitrosyl-sulphuric acid and nitric acid,

$$2NO_2 + H_2SO_4 = NO_2.SO_3H + HNO_3.$$

**724. Detection.**—Nitrogen tetroxide is recognisable by its odour and its brown colour and its reaction with water to give a colourless liquid (distinction from bromine and chromyl chloride). It is an oxidising agent and liberates iodine from potassium iodide.

## Nitrogen Pentoxide.

**725. Preparation.**—(i.) Nitrogen pentoxide is most readily made by the action of phosphorus pentoxide on pure water-free nitric acid. The latter is mixed in a cooled distilling flask with twice its weight of the former. The flask is then heated to 60–70° C. and the nitrogen pentoxide is distilled over in a current of air and condenses as a yellow solid in a series of well-cooled wash-bottles,

$$P_2O_5 + 2HNO_3 = N_2O_5 + 2HPO_3.$$

(ii.) The action of chlorine on dry silver nitrate produces nitrogen pentoxide,

$$4AgNO_3 + 2Cl_2 = 2N_2O_5 + 4AgCl + O_2.$$

Nitrogen pentoxide forms white crystals (m.p. 29·5° C.). It begins to decompose above its melting point and explodes when rapidly heated, $2N_2O_5 = 2N_2O_4 + O_2$.

With water it forms nitric acid, much heat being evolved,

$$N_2O_5 + H_2O = 2HNO_3.$$

**726. Nitrogen Trioxide $NO_3$** has been prepared by the action of the glow discharge on nitrogen dioxide and oxygen. It is a colourless solid unstable above − 140° C.

## Oxyacids of Nitrogen

**727. Hyponitrous Acid $H_2N_2O_2$, HO—N=N—OH.**—Hyponitrous acid and hyponitrites are prepared, as a rule, by reduction of nitrites.

Thus, if a cold solution of sodium nitrite is reduced by sodium amalgam the hyponitrite is formed,

$$2NaNO_2 + 4H = Na_2N_2O_2 + 2H_2O.$$

The addition of silver nitrate to the neutralised solution precipitates silver hyponitrite, which may be rubbed in a mortar with cold dilute HCl and the solution of hyponitrous acid filtered off,

$$Ag_2N_2O_2 + 2HCl = H_2N_2O_2 + 2AgCl.$$

Hyponitrites are also prepared by the action of sulphites upon nitrites.

Hyponitrous acid in the pure state forms white leaflets, which explode when rubbed. The solution is a very weak acid which does not decompose carbonates. It decomposes slowly in air into nitrous and nitric acids,

$$2H_2N_2O_2 + 3O_2 = 2HNO_3 + 2HNO_2.$$

When boiled it gives nitrous oxide,

$$H_2N_2O_2 = H_2O + N_2O.$$

It is a reducing agent, being oxidised by permanganate to nitrates.

Its structural formula is indicated by the decomposition of its ethyl ester

$$(C_2H_5)_2N_2O_2 \rightarrow \underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\text{Aldehyde.}}{C_2H_4O} + \underset{\text{Nitrogen.}}{N_2}.$$

which shows that it contains the azo-group − N = N − and its formula is therefore probably HO − N = N − OH.

**728. Hydronitrites.**—Sodium hydronitrite $Na_2NO_2$ has been made by the interaction of sodium nitrite and sodium dissolved in liquid ammonia. It is unstable, decomposing violently at 100–130° C. The acid $H_2NO_2$ has not been isolated.

## Nitrous Acid $HNO_2$.

**729. Preparation of Nitrous Acid.**—Nitrous acid is unstable and cannot be preserved, but its salts, the nitrites, are stable compounds.

Nitrous acid is formed—

(1) By the action of nitrogen trioxide on water at 0° C.,

$$N_2O_3 + H_2O = 2HNO_2.$$

(2) Nitrites when treated with dilute acids yield nitrous acid, which almost immediately begins to decompose. The pure dilute acid is obtained when barium nitrite solution is decomposed by the theoretical quantity of ice-cold dilute sulphuric acid. In this way a roughly fifth-normal solution can be obtained.

$$Ba(NO_2)_2 + H_2SO_4 = BaSO_4\downarrow + 2HNO_2.$$

The acid may be decanted or filtered from the insoluble barium sulphate.

**730. Formula.**—Nitrous acid has the formula $HNO_2$ as shown by its monobasic character and its formation from nitrogen trioxide and water. The behaviour of some of its derivatives indicate the structure

$$H - N\begin{matrix}=O\\ \searrow O\end{matrix}$$

while that of others indicates, $HO - N = O$

**731. Properties of Nitrous Acid.**—Nitrous acid forms a blue solution which rapidly decomposes even in the cold, evolving nitric oxide and leaving dilute nitric acid,

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O.$$

At higher temperatures nitrogen peroxide and nitric oxide are evolved,

$$2HNO_2 \rightleftharpoons NO + NO_2 + H_2O.$$

Nitrous acid is a very reactive substance. It acts both as a reducing agent and an oxidising agent.

Thus most *oxidising agents* (permanganates, dichromates, chlorine, bromine) convert it into nitric acid, *e.g.*,

$$HNO_2 + Br_2 + H_2O \rightleftharpoons HNO_3 + 2HBr.$$

Nitrites may be titrated with permanganate, the reaction being

$$5KNO_2 + 2KMnO_4 + 4H_2SO_4 = 5KNO_3 + 2KHSO_4 + 2MnSO_4 + 3H_2O.$$



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*Reducing agents* convert nitrous acid into nitric oxide. Thus stannous chloride reduces it,

$$SnCl_2 + 2HCl + 2HNO_2 = SnCl_4 + 2H_2O + 2NO,$$

as do also sulphur dioxide and hydrogen sulphide.

Nitrous acid reacts with ammonia and with many substances containing the $-NH_2$ group, liberating water and nitrogen (§ 679 (1)),

$$NH_3 + HNO_2 = NH_4NO_2 = N_2 + 2H_2O.$$

Thus nitrous acid and urea give carbon dioxide, water and nitrogen,

$$CO\begin{<}NH_2\\NH_2\end{>} + 2HNO_2 = CO_2 + 3H_2O + 2N_2$$

With certain organic amines (the aromatic amines in particular) diazonium compounds containing the $-N^+\equiv N$ group are produced,

$$C_6H_5NH_3Cl + HNO_2 = \left[C_6H_5 - N \equiv N\right]^+ Cl^- + 2H_2O.$$

Aniline hydrochloride. Benzenediazonium chloride.

These diazonium compounds give dyestuffs of intense colour with certain amines and phenols, and a sensitive test for nitrites depends on their reaction with metaphenylene-diamine hydrochloride, $C_6H_4(NH_2)_2HCl$, to form a dyestuff—Bismarck brown.

**732. Nitrites.**—The nitrites of the alkali metals are prepared by heating the nitrates with or without the addition of a reducing agent (§ 242), but they are chiefly prepared from the diluted oxides of nitrogen left over in the preparation of nitric acid by oxidation of ammonia (§ 738).

They are for the most part very soluble salts. All nitrites except those of sodium and potassium are decomposed by heat into oxides of nitrogen and a metallic oxide. With acids nitrous acid is liberated (*v.* § 729). Numerous complex nitrites are known, among which are notable the cobalti-nitrites (§ 1192). Sodium nitrite (§ 242) finds much use in the dye industry.

## Nitric Acid $HNO_3$

**733. History.**—Nitric acid is first described in the works attributed to Geber, as being made by the distillation of nitre, blue vitriol and alum. The latter, when heated, formed sulphuric acid, which reacted with the nitre. Geber flourished in the eighth century A.D., but it is not certain that the Latin works attributed to him are earlier than *c.* 1100. The preparation from sulphuric acid and nitrates was originated by Glauber in 1648.

Lavoisier showed that the acid contained oxygen, and later that it was composed of nitrogen, hydrogen and oxygen.

**734. Occurrence.**—Free nitric acid is formed by lightning flashes, which bring about the combination of the oxygen and nitrogen of the air according to the reactions outlined on pp. 537–539 below. These traces of nitric acid, carried down by rain water, afford one of the sources of soil nitrogen.

**735. Preparation of Nitric Acid.**

(1) Nitric acid is made on the laboratory scale by the distillation of a nitrate, usually of potassium, with sulphuric acid. Equal weights may be used and the acid distilled over into a cooled receiver,

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

The product contains some dissolved nitrogen tetroxide, which colours it yellow, and usually also a little water. It is purified by mixing it with concentrated sulphuric acid, distilling again, and 'washing' the nitrogen tetroxide out of the distillate by blowing a current of dry air through it.

(2) Nitric acid is made on the large scale by oxidising ammonia

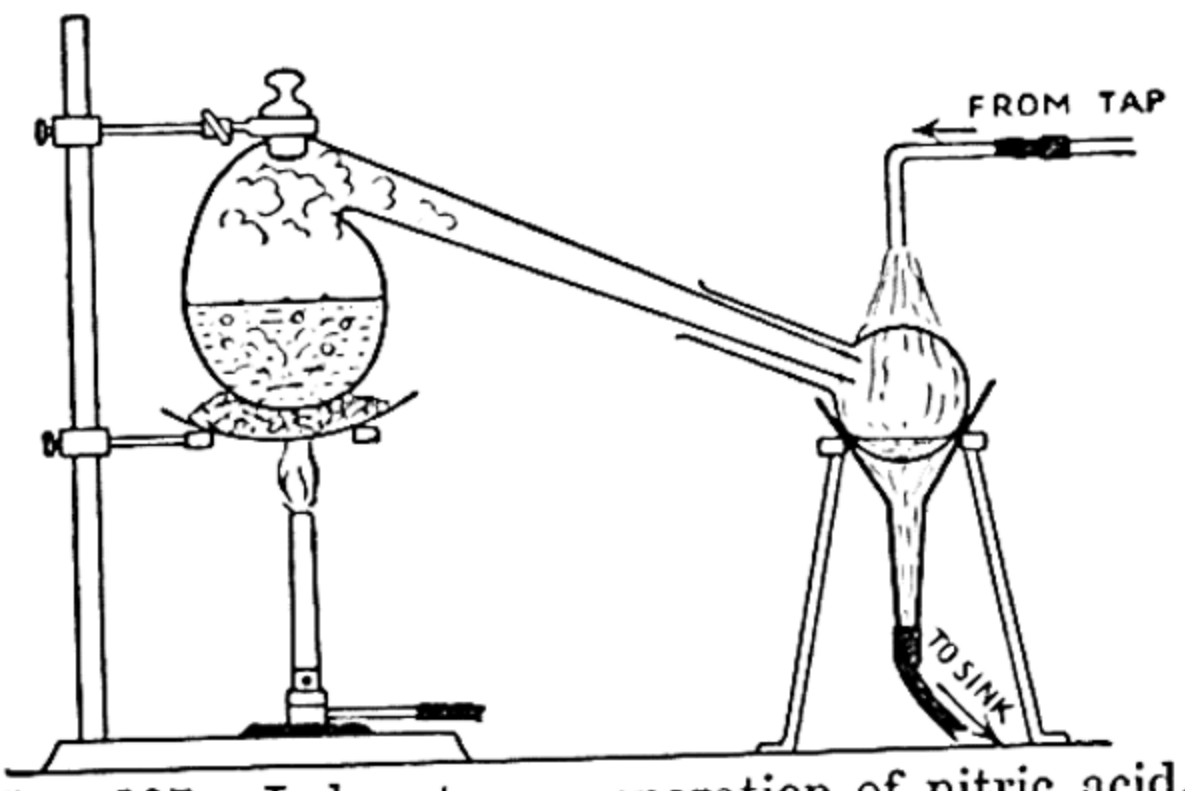


FIG. 137.—Laboratory preparation of nitric acid.

and by the direct combination of nitrogen and oxygen in presence of water. These important processes are discussed below.

**736. Manufacture of Nitric Acid from Sodium Nitrate.**—Sodium nitrate is obtained in great quantities from the nitre beds of Chile and Peru (§ 242), and this salt is one of the chief sources of nitric acid.

On the commercial scale approximately equal weights of 'oil of vitriol' (crude sulphuric acid) and sodium nitrate are distilled in a cast-iron retort. The reaction takes place as described,

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3,$$

in the last section, and nitric acid is driven off.

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The greatest part of the vapour is condensed in water-cooled earthenware or silica pipes. The uncondensed gases are passed over stoneware balls contained in a small tower down which water flows, being continually circulated until it becomes fairly strong acid.

The residue in the retort is mostly sodium pyrosulphate, arising from the decomposition of the sodium hydrogen sulphate first formed,

$$2NaHSO_4 = Na_2S_2O_7 + H_2O.$$

This residue, being readily fusible, is run out of the retort in a

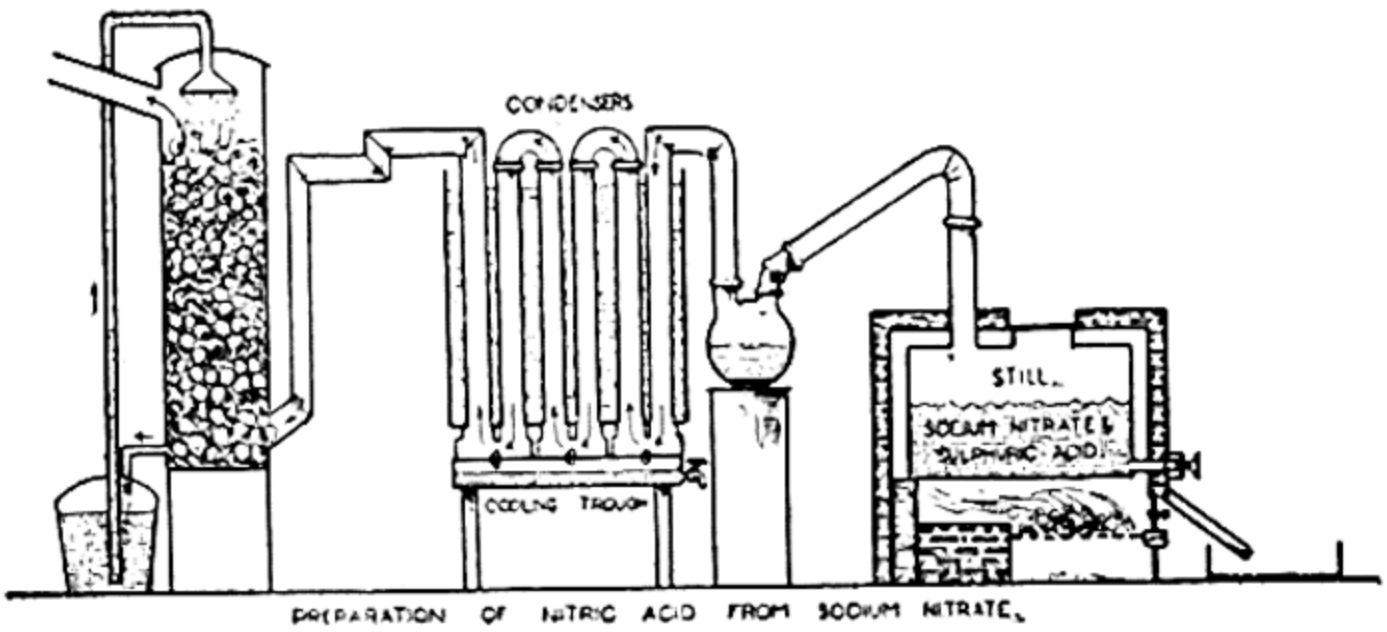


FIG. 138.—Manufacture of nitric acid from sodium nitrate.

liquid condition. It was a former practice to conduct the distillation at such a high temperature that the reaction to normal sodium sulphate took place,

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3,$$

thereby obtaining twice as much nitric acid from a given weight of sulphuric acid. This is no longer done, for the labour of digging out the infusible sodium sulphate is such that it pays better to use more acid and empty the retorts by simply opening a plug.

**737. Manufacture of Nitric Acid directly from Air and Water.**—When a mixture of nitrogen and oxygen is subjected to a very high temperature some nitric oxide is formed according to the equation,

$$N_2 + O_2 \rightleftharpoons 2NO - 43{,}200 \text{ cals.}$$

Since heat is absorbed when nitric oxide is formed, the percentage of nitric oxide in the mixture at equilibrium becomes greater as the temperature becomes higher. (Law of van't Hoff and Le Chatelier, § 111.) It is only at temperatures between 2,000° C. and 3,000° C. that a useful yield of nitric oxide is obtainable. The only means of obtaining such a temperature cheaply is the use of the electric arc. If the nitric oxide so formed be allowed to cool slowly the equilibrium shifts back to the left and only oxygen and nitrogen remain, but if the gases are cooled very quickly to a temperature below 1,000° C. the equilibrium has not time to readjust itself entirely. The

rate of decomposition of nitric oxide below 1,000° C. is so slow as to be immeasurable. The problem is then to heat air to the highest temperature possible and cool it quickly. The method adopted varies somewhat. The Birkeland-Eyde process, described below, is now but little used, but is worth describing as having been the first method used for the fixation of atmospheric nitrogen.

A large electric arc is spread into a thin disc of flame by the action of an electro-magnet. The arc between two electrodes carries a current and therefore tends to move in a magnetic field. The direction of the current being

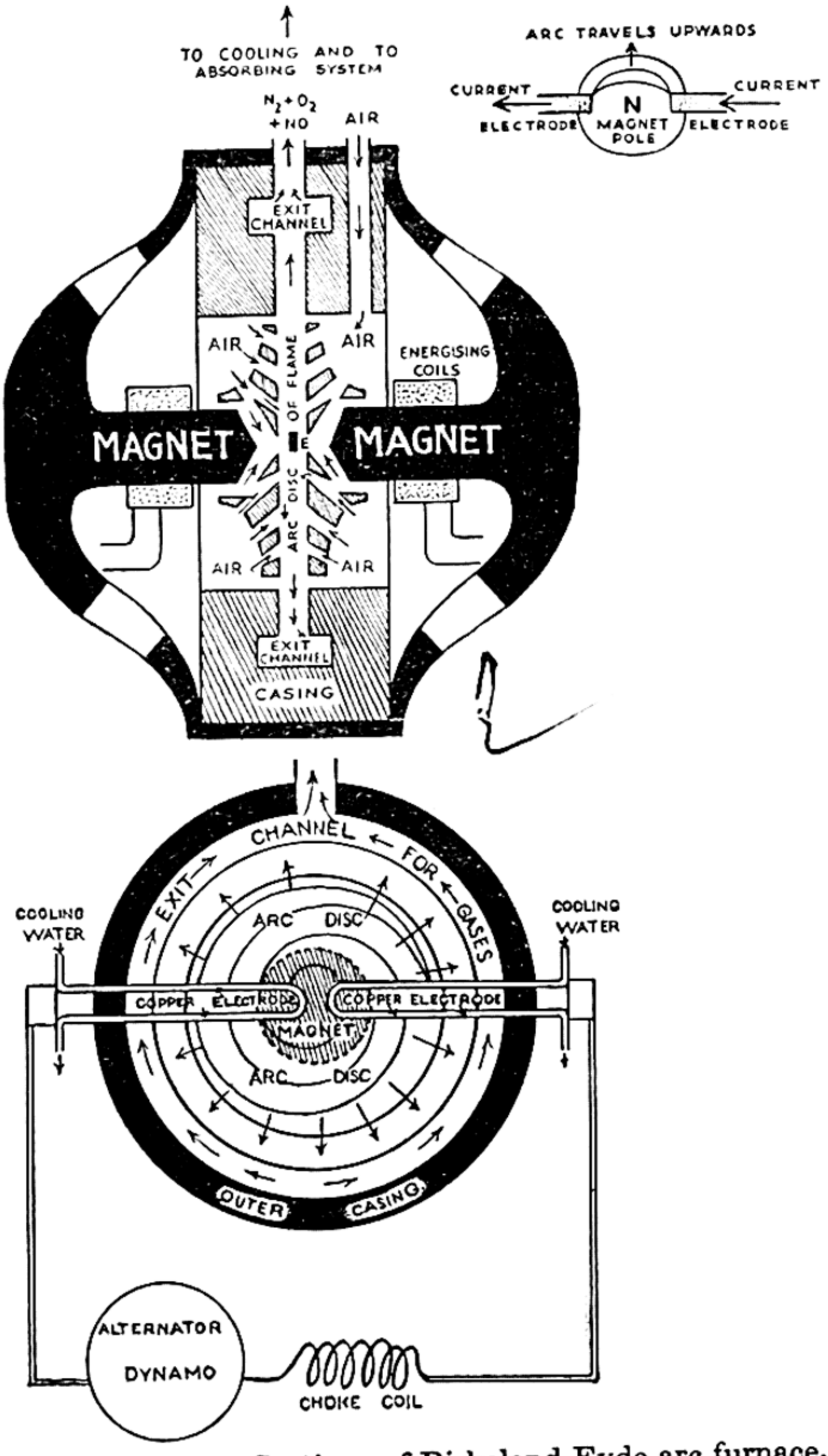


FIG. 139.—Sections of Birkeland-Eyde arc furnace.

reversed many times a second, the arc travels alternately in each direction and spreads into a thin, intensely hot flame, some 6 feet in diameter. Air is directed into this sheet of flame and forms a proportion of nitric oxide (*c.* 1 per cent.). This is carried off and cooled by passage through the tubes of a series of fire-tube boilers, which raise the steam necessary for all the operations carried on at the works (except, of course, the generation of the electricity). The mixture of nitric oxide and air is converted into nitric acid as in § 738.

**738. Manufacture of Nitric Acid from Ammonia.**—This is now the most important method of manufacture. If a mixture of ammonia gas and air be passed through a heated tube nitrogen and water are the normal products,

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O.$$

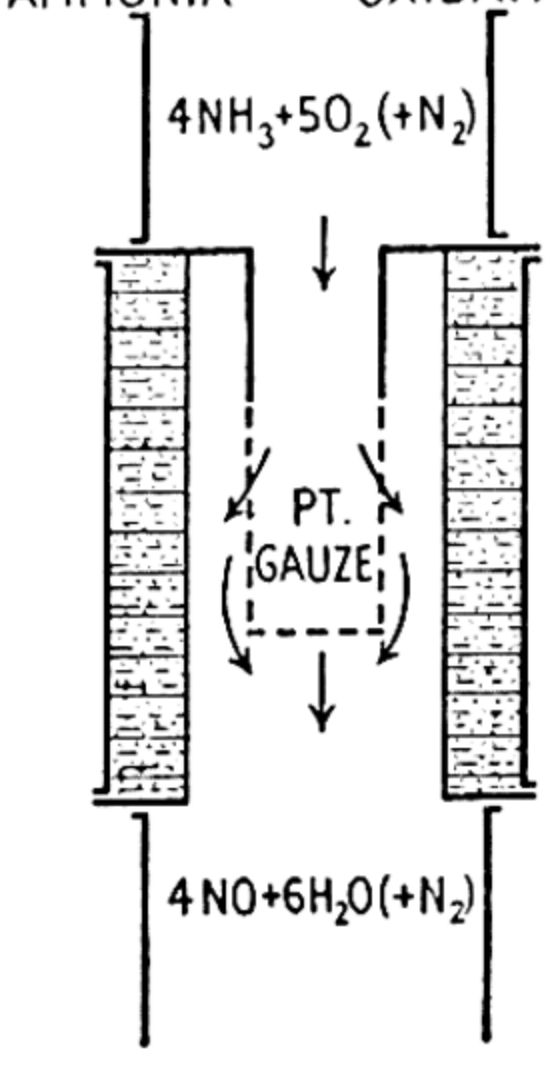


FIG. 140.—Catalytic oxidation of ammonia.

But if the tube contains metallic platinum in any form the reaction takes another course and nitric oxide is produced,

$$4NH_3 + 5O_2 = 4NO + 6H_2O.$$

On the commercial scale synthetic ammonia, made as described in § 689, may be readily oxidised to nitric acid. A mixture of ammonia and air in the proportion of about one volume of ammonia to nine of air is passed through a cylinder of heated platinum wire gauze (Fig. 140), when it is rapidly and completely oxidised to nitric oxide. The gases, when they have cooled to 200°–250° C., undergo a further reaction, nitrogen peroxide being produced,

$$2NO + O_2 = 2NO_2.$$

This is then further cooled and passed up a series of granite towers filled with broken quartz, over which water flows. The acid formed in the third tower passes to the second, and thence to the first, finally reaching a strength of about 40–50 per cent. The reactions are

(1) $$2NO_2 + H_2O = HNO_3 + HNO_2.$$

The nitrous acid mostly decomposes in the first two towers, forming nitric acid and nitric oxide,

(2) $$3HNO_2 = 2NO + HNO_3 + H_2O.$$

The nitric oxide so formed is again oxidised by the oxygen in the gases to nitrogen peroxide, which is absorbed according to equation (1) above. As it is difficult to convert the whole of the gases into nitric acid they are led to two towers, fed with sodium carbonate,

where sodium nitrite is produced, a substance much used in the dye industry.

$$Na_2CO_3 + 2NO + O_2 = NaNO_2 + NaNO_3 + CO_2.$$

The nitric acid may be concentrated by distillation or may be converted into calcium nitrate, which is sold as a fertiliser.

The process may readily be illustrated on the laboratory scale by means of the apparatus shown in Fig. 141. Air is drawn through ammonia solution (2 parts ·880 ammonia to 1 of water) and the gases are passed through three discs of platinum gauze, 1 mm. apart. These require heating to start the reaction, and then are maintained at a red heat by the heat of reaction. Nitric acid condenses in the cooled receiver.

**739. Physical Properties.**—Liquid nitric acid is not obtainable in a state of complete purity owing to a slight degree of decomposition which always takes place even below its boiling point. The purest acid is a colourless fuming liquid, which has a specific gravity of 1·52, and which freezes at — 47° C. and boils at 86° C. The nitric acid commonly sold is of three kinds. These include fuming nitric

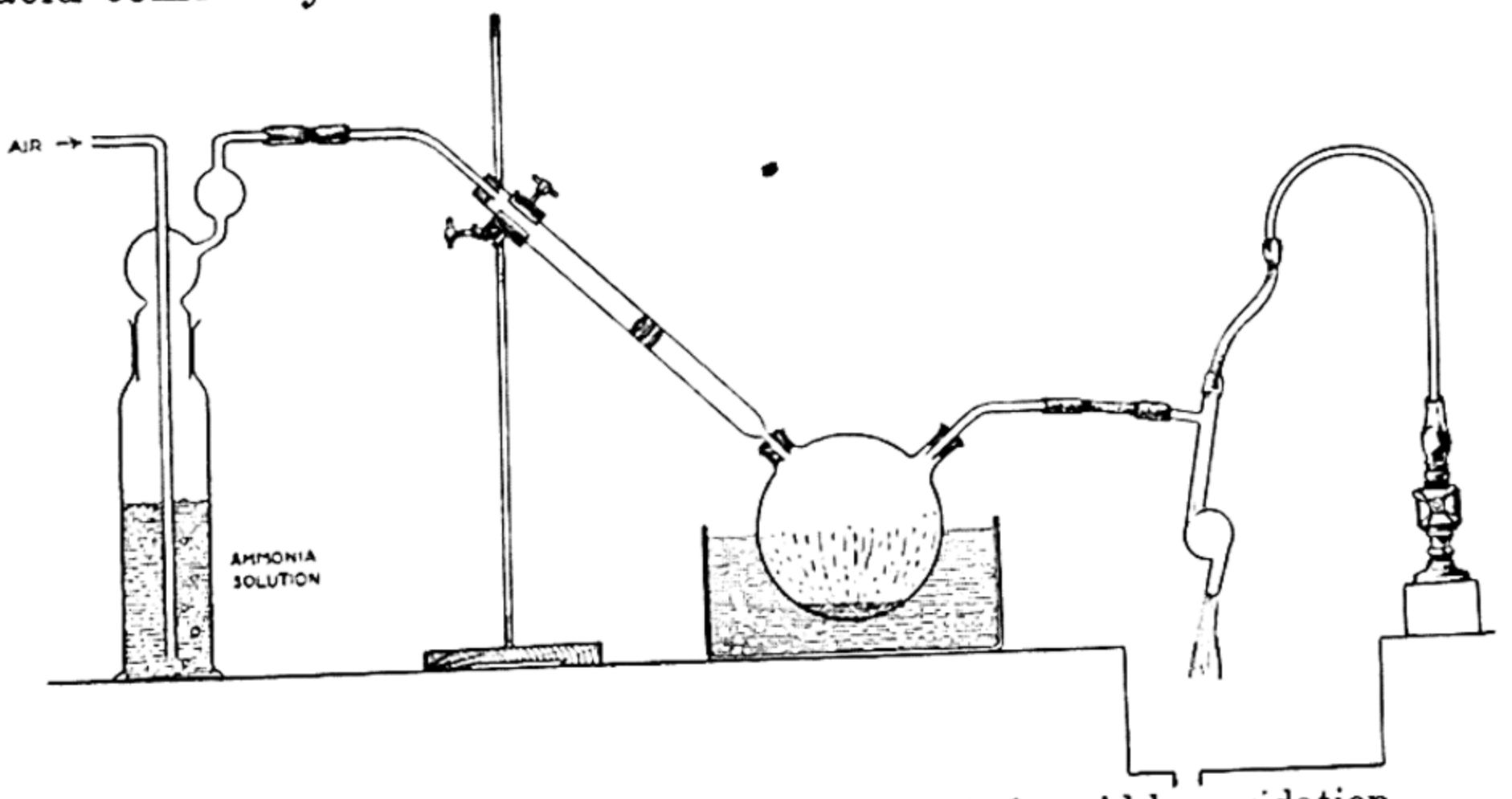


FIG. 141.—Demonstration of synthesis of nitric acid by oxidation of ammonia.

acid, which contains dissolved nitrogen peroxide and is yellow or red in colour, and 'concentrated nitric acid,' of density 1·5, containing about 98 per cent. $HNO_3$. The ordinary 'strong nitric acid' is of density 1·4 and contains about 65 per cent. of $HNO_3$. Certain mixtures of nitric acid and water boil at temperatures higher than either constituent. A maximum occurs with the liquid containing 68 per cent. of nitric acid, which boils at 120·5° C. under atmospheric pressure and consequently is a constant boiling mixture (*v.* § 1055).

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Nitric acid is miscible in water in all proportions.

Most organic substances react with it, but it is a good solvent for those which do not do so.

**740. Chemical Properties.**—Nitric acid is readily decomposed by heat, yielding nitrogen peroxide, oxygen and water,

$$4HNO_3 = 2H_2O + O_2 + 4NO_2.$$

The reaction is easily shown by arranging a clay pipe so that the stem is heated by a Bunsen burner, while the mouth-piece dips beneath water. If nitric acid is poured into the bowl the gases issue from the stem ; the nitrogen peroxide reacts with the water (§ 723), while the oxygen may be collected.

Nitric acid has three modes of chemical behaviour :—

(*a*) As an acid.

(*b*) As an oxidising agent.

(*c*) As a nitrating agent.

**741. Acidic Properties of Nitric Acid.**—Nitric acid is a strong acid, by which is meant that solutions of the acid contain a high proportion of hydrogen ion. It is not, however, the strongest. Hydrogen chloride, bromide and iodide are completely dissociated in solution, whereas solutions of nitric and sulphuric acid can be shown, by the Raman effect (§ 103a), to contain some undissociated acid.

It displays the normal properties of an acid (§ 163) in all cases where its oxidising action does not come into play. Thus it reacts with basic oxides, hydroxides and carbonates in the usual way unless the metallic radical has reducing properties (*e.g.*, ferrous or stannous compounds).

Thus with cupric oxide it gives cupric nitrate and water,

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O,$$

but with ferrous hydroxide, ferric nitrate, nitric oxide, and water are formed,

$$6Fe(OH)_2 + 20HNO_3 = 6Fe(NO_3)_3 + 2NO + 16H_2O.$$

Its reactions with metals are abnormal on account of the reduction of the acid. These are discussed below (§ 744).

Since nitric acid is readily volatile it is easily expelled from combination by heating its salts with less volatile acids, *e.g.*, sulphuric, phosphoric, boric acid. An equilibrium is set up,

$$NaNO_3 + HA \rightleftharpoons NaA + HNO_3.$$

The continual removal of nitric acid by volatilisation and the consequent further reaction of nitrate and acid (restoring the equilibrium) causes the reaction of a nitrate with even so weak an acid as boric acid to be complete.

**742. Oxidising Properties of Nitric Acid.**—Nitric acid is a most powerful oxidising agent, and its reactions with reducing agents follow several courses.

Concentrated nitric acid always produces nitrogen peroxide when it reacts with a reducing agent,

$$2HNO_3 + X = H_2O + 2NO_2 + XO,$$

but both dilute and moderately concentrated acid also produce nitric oxide,

$$2HNO_3 + 3X = H_2O + 2NO + 3XO.$$

Besides the above gases, nitrogen trioxide and, less commonly, nitrous oxide, nitrogen, ammonium nitrate and hydroxylamine are formed as products of the reaction of nitric acid on reducing agents.

**743. Action of Nitric Acid on Non-metallic Elements.**—Nitric acid reacts with most non-metals, nitrogen, oxygen, chlorine and bromine being the only ones unaffected. The highest oxides are usually formed and these usually combine with the water produced in the reaction to form oxyacids.

Thus with heated nitric acid phosphorus forms phosphoric acid,

$$P + 5HNO_3 = H_3PO_4 + 5NO_2 + H_2O.$$

Sulphur gives sulphuric acid when boiled with nitric acid,

$$S + 6HNO_3 = H_2SO_4 + 6NO_2 + 2H_2O.$$

Iodine gives iodic acid ; boron, boric acid ; arsenic, arsenic acid. Silicon and carbon give their dioxides, which unlike most other higher oxides of non-metals do not combine with water to form oxyacids at the temperature at which the reaction occurs.

**744. Action of Nitric Acid on Metals.**—Nitric acid reacts with all metals except gold, platinum, iridium, rhodium, tantalum and titanium. Certain metals are rendered 'passive' or protected by oxide films from its action (*v.* § 1149).

Nitric acid does not give hydrogen with metals, except in one case, *i.e.*, when magnesium reacts with dilute nitric acid. In other cases it is sometimes considered that a metallic nitrate and hydrogen are formed by the reaction of the acid and the metal and that the 'nascent' hydrogen (§ 192) then reacts with the remaining acid, producing some reduction product. There is, however, very little evidence for this or any other theory of the mode of reaction of nitric acid and metals.

The chief products formed are nitrogen peroxide and nitric oxide ; but nitrous oxide, hyponitrous acid, nitrogen, ammonium nitrate and hydroxylamine may all be formed. Nitrous acid appears to act

catalytically, for pure nitric acid free from this substance reacts but slowly with metals.

The main reaction with the majority of metals and acid of moderate strength results in the formation of a nitrate and nitric oxide. The reaction may be formulated in two stages, in order to arrive at the correct equation, but it must not be assumed that these partial equations represent reactions which actually take place.

(1)
$$\begin{aligned} 3Cu + 6HNO_3 &= 3Cu(NO_3)_2 + 6H \\ 6H + 2HNO_3 &= 4H_2O + 2NO \\ \hline 3Cu + 8HNO_3 &= 3Cu(NO_3)_2 + 4H_2O + 2NO. \end{aligned}$$

The use of more concentrated acid brings about some formation of nitrogen peroxide, but this rarely appears to be the sole product. Iron and concentrated nitric acid, however, yield almost exclusively nitrogen peroxide and ferric nitrate,

$$\begin{aligned} Fe + 3HNO_3 &= Fe(NO_3)_3 + 3H \\ 3H + 3HNO_3 &= 3H_2O + 3NO_2 \\ \hline Fe + 6HNO_3 &= Fe(NO_3)_3 + 3H_2O + 3NO_2. \end{aligned}$$

In the case of the more electropositive metals, such as zinc, tin, lead, iron, magnesium, the use of dilute acid may bring about reduction to nitrous oxide, nitrogen, ammonium nitrate, etc. The third case is of interest and may be illustrated by equations :

$$\begin{aligned} 4Zn + 8HNO_3 &= 4Zn(NO_3)_2 + 8H \\ HNO_3 + 8H &= NH_3 + 3H_2O \\ NH_3 + HNO_3 &= NH_4NO_3. \\ \hline 4Zn + 10HNO_3 &= 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O. \end{aligned}$$

Equations for the formation of any reduction product may be devised by (1) writing the equation for the reaction of nitric acid and hydrogen to form the reduction product and water; (2) writing an equation for the reaction of the metal and acid to form the necessary hydrogen for the above equation; (3) adding the two equations, omitting substances which appear on each side. Such equations are not, however, as a rule, very useful, for it is rarely that any such change is simple enough to be represented by a single equation.

To sum up, the character of the reduction product is conditioned by the concentration of the acid and the more or less electropositive character of the metal. Concentrated acid always evolves nitrogen peroxide, for it oxidises nitric oxide to the latter gas. More dilute acid (*c.* 10–30 per cent.) evolves mostly nitric oxide. The more electropositive metals reduce the well-diluted acid to ammonium salts, etc.

**745. Oxidising Action of Nitric Acid on Compounds.**—Nitric acid reacts with all reducing agents, among which we may mention

hydrogen sulphide, sulphur dioxide, hydrogen chloride, bromide and iodide, ferrous salts, stannous salts, arsenites, etc., etc. The reactions cannot be discussed here in detail, but are considered under the heading of the several reducing agents.

In general we may write the equation of the reaction of the reducing agent with oxygen, and the reaction of nitric acid to form the appropriate oxide of nitrogen and the oxygen required for this. These equations are added together. It does not by any means follow that the reaction really takes place in these stages, which are only a mathematical convention. Thus we may consider the reaction of acidified ferrous sulphate with nitric acid, forming ferric sulphate and nitric oxide,

$$2HNO_3 = H_2O + 2NO + 3O$$
$$6FeSO_4 + 3H_2SO_4 + 3O = 3Fe_2(SO_4)_3 + 3H_2O$$
$$\overline{6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.}$$

As a second example we may take the action of nitric acid on sulphur dioxide, forming sulphuric acid and nitrogen peroxide,

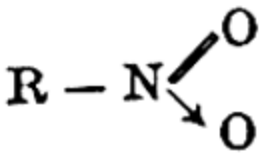
$$SO_2 + O = SO_3$$
$$SO_3 + H_2O = H_2SO_4$$
$$2HNO_3 = H_2O + 2NO_2 + O$$
$$\overline{SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2.}$$

**746. Action of Nitric Acid on Organic Compounds.**—Nitric acid oxidises many organic compounds to carbon dioxide and water, the reaction sometimes proceeding with explosive violence. Thus mixtures of concentrated nitric acid and alcohol may explode if warmed. If a little warm concentrated nitric acid (S.G. 1·5) is poured on dry sawdust the latter will often burst into flame.

Nitric acid does not always act as violently as this, and in these cases it usually forms *nitro-compounds*, which are of great technical importance. Thus benzene treated with nitric acid to which sulphuric acid has been added (as a drying agent) yields nitro-benzene,

$$C_6H_6 + HNO_3 = C_6H_5 . NO_2 + H_2O.$$

The nitro-group $- NO_2$ is not the same as the nitrite group $- NO_2$. Thus there are two quite different compounds, nitro-ethane and ethyl nitrite, both of formula $C_2H_5 . NO_2$. Their structural formulæ are probably



Nitro-compound.

$$R - O - N = O.$$

Nitrite.

**747. Uses of Nitric Acid in the Laboratory.**—Nitric acid is used for most purposes where an oxidising agent is required, notably in the following cases :—

(1) Preparation of the oxides and oxyacids of non-metals (§ 743).

(2) The preparation of metallic oxides from metals *via* their nitrates (§§ 744, 750).

(3) The solution of insoluble sulphides, such as iron pyrites, copper sulphide, etc. (§ 905), by oxidation to sulphates.

(4) The production of aqua regia (§ 1044 (8) ).

(5) In organic chemistry, in the preparation of oxalic acid, in the making of nitro-compounds, etc.

**748. Uses of Nitric Acid in Industry.**—Nitric acid finds uses in numerous industries, among which may be named :—

(1) The manufacture of nitro-compounds and of ammonium nitrate in the explosives industry.

(2) The manufacture of nitro-compounds, as both intermediate and final products in the dye industry.

(3) Use of nitric acid for cleaning metals before electro-plating.

(4) Numerous minor uses in the chemical industries.

**749. Detection and Estimation of Nitric Acid and Nitrates.**—The 'brown ring' test is the most delicate method of detecting nitric acid or nitrates. Nitrites also give the test. They may, however, be distinguished from nitrates by the fact that they give the coloration with *dilute* sulphuric and without heating.

The brown ring test is performed by mixing the suspected solution with an excess of sulphuric acid, heating the mixture and cooling thoroughly; ferrous sulphate solution is then carefully poured down the side of the test tube so as to rest as a layer on the surface of the acid. A brown ring or layer is produced where the two liquids meet.

Alternatively, the supposed nitrate and the ferrous sulphate may be mixed and sulphuric acid poured down the side of the test-tube.

Reaction takes place between the nitric acid, ferrous sulphate and sulphuric acid, forming nitric oxide (§ 712 (3) ), which then forms the dark-coloured compound, $FeSO_4.NO$.

The sulphuric acid and ferrous sulphate solution being in separate layers produce only local heating where they meet, and this is soon dissipated by conduction to the cold liquid above and below. If the solutions were merely mixed the temperature would be too high for the formation of the unstable $FeSO_4.NO$.

A second test is the addition of a solution of 'nitron,' a complex organic base, which gives with nitric acid or nitrates a precipitate of its insoluble nitrate.

*Estimation*—Nitric acid and nitrates are difficult to estimate. Free nitric acid may, of course, be titrated with alkali. The most

usual method of determining nitrates is to reduce them to ammonia by heating them in alkaline solution with Devarda's alloy (§ 687), which evolves nascent hydrogen at a high potential. The ammonia formed,

$$KNO_3 + 8H = KOH + NH_3 + 2H_2O,$$

is distilled over into standard acid and from the reduction of the strength of the acid the quantity of nitrate present is calculated.

**750. Nitrates.**—The nitrates of the metals are all freely soluble in water. When heated they decompose. Ammonium nitrate forms nitrous oxide and water (§ 707); the nitrates of the alkali-metals form the nitrite and oxygen (§ 242), while the nitrates of the heavy metals give nitrogen peroxide, oxygen and the oxide of the metal (§ 720). When heated with concentrated sulphuric acid they yield nitric acid (§ 736). Hot concentrated hydrochloric acid converts them into chlorides, evolving nitrosyl chloride and chlorine (cf. § 1044 (8).

Mixtures of nitrates and combustibles burn violently, often with explosion (cf. § 263 on gunpowder).

*Pernitrates.*—A silver pernitrate, $AgNO_5$, has been reported. It is prepared by the electrolytic oxidation of silver nitrate. A solution of pernitric acid is stated to have been made by the action of hydrogen peroxide on nitrous acid.

**751. Halides of Nitrogen.**—The most important of these is $NCl_3$, nitrogen trichloride. Nitrogen trifluoride $NF_3$ has recently been prepared, as has also the iodide $NI_3$. The so-called nitrogen iodide $N_2H_3I_3$ is a compound of this halide, $NH_3 . NI_3$. The compounds, $N_3Cl$, $N_3Br$, $N_3I$, chlorazide, bromazide, iodine azide also exist. All the nitrogen halides, other than fluorides, are unstable and explosive.

**752. Nitrogen Trifluoride** is obtained by electrolysing fused anhydrous ammonium hydrogen fluoride,

$$2(NH_4)HF_2 + 12F = 2NF_3 + 5H_2F_2.$$

The fluorine formed attacks the ammonium salt. It is a colourless gas insoluble in water. It is reactive, but much more stable than other nitrogen halides. $NHF_2$ and $NH_2F$ have also been prepared.

**753. Nitrogen Trichloride** is formed by the action of chlorine on an ammonium salt. Its highly explosive character renders its preparation by the student most inadvisable.

When a jar of chlorine is inverted over saturated ammonium chloride, nitrogen trichloride separates as oily droplets,

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl.$$

It may be safely handled in solution in benzene, and if acidified solutions of bleaching powder and ammonium chloride are shaken with benzene, the nitrogen chloride passes into solution in the benzene as soon as it is formed, and can be safely handled.[1]

[1] The preparation should on no account be attempted without consulting the original paper. Hentschel. *Berichte*, 1897, **30**, 1434, 1792, 2642.

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Nitrogen chloride is an oily liquid and an extremely sensitive explosive. Gentle heat, strong light, or contact with many oily substances cause it to explode. Several eminent chemists, including Sir Humphry Davy, have been maimed by the explosions of this substance.

**754. Nitrogen Iodide.**—A substance which was for long regarded as nitrogen iodide is prepared by the action of iodine on ammonia. Its composition does not appear certain, but it may be $NH_3 . NI_3$, a compound of ammonia and true nitrogen iodido,

$$2NH_4OH + I_2 = NH_4OI + NH_4I + H_2O$$
$$3NH_4OI \rightleftharpoons NH_3 . NI_3 + NH_4OH + 2H_2O.$$

It is extremely sensitive to shock, the dry substance exploding even by contact with a feather. For this reason it should be prepared only in the smallest quantities. Nitrogen iodide is an oxidising agent.

The true nitrogen iodide, $NI_3$, has been recently isolated by the reaction of dry ammonia and potassium dibromoiodide.

$$4NH_3 + 3KIBr_2 = 3KBr + 3NH_4Br + NI_3.$$

It is a black explosive substance.

**755. Chloramine $NH_2Cl$.**—Monochloramine is obtained by distilling normal solutions of potassium hypochlorite and ammonia under reduced pressure at 30–40° C.

$$KOCl + NH_3 = NH_2Cl + KOH.$$

A 10–12 per cent. solution is obtained. The pure substance is very unstable, exploding violently at temperatures above — 50° C. Chloramine is a powerful oxidising agent. The intense germicidal action of sodium hypochlorite (which is far greater than that of the chlorine it contains) is due to its reaction with the ammonia and amino-compounds always present in contaminated water. The chloramine so formed effectively destroys the bacteria, etc., which swarm in wells contaminated by sewage, in unfiltered public swimming baths, etc. Organic compounds of chloramine are used as antiseptics in surgery.

**756. Nitrogen Sulphide $N_4S_4$** is formed by the action of ammonia gas on sulphur monochloride in solution in chloroform. The nitrogen sulphide is precipitated on addition of alcohol.

It forms orange-yellow crystals melting at 185° C. and decomposing explosively at higher temperatures.

A compound $(HSN)_4$ has also been described.

# CHAPTER XVIII

## PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH

**757. The Elements of Group V.**—Group V. contains the elements:

| A Sub-group. | B Sub-group. |
|---|---|
| | Nitrogen. |
| | Phosphorus. |
| Vanadium. | |
| | Arsenic. |
| Niobium (Columbium). | |
| | Antimony. |
| Tantalum. | |
| | Bismuth. |
| Protoactinium. | |

The A sub-group is discussed in § 843.

In the B sub-group definite resemblances are noticeable between nitrogen and phosphorus, though these are not so strong as those between phosphorus and arsenic or arsenic and antimony. It is usual in all groups for the lightest element to resemble the subsequent ones less closely than they resemble each other.

Phosphorus resembles nitrogen in a good many respects.

Both elements form a basic hydride, though phosphine $PH_3$ is much less basic than ammonia $NH_3$. The oxides $N_2O_3$, $N_2O_4$, $N_2O_5$ have some chemical resemblance to $P_2O_3$, $P_2O_4$, $P_2O_5$. The acids, nitric acid $HNO_3$, and meta-phosphoric acid $HPO_3$, have similar formulæ, but few other common properties. The other acids of phosphorus find no analogy in the nitrogen compounds. The halides of the two elements show no resemblance.

On the other hand, phosphorus and arsenic are closely alike. The gaseous hydrides of both elements are strong reducing agents. The phosphites, phosphates, arsenites and arsenates are very similar in their reactions. The halides are also similar in appearance and properties.

Phosphorus and nitrogen can both exert a valency of five.

The quinquevalent compounds of phosphorus are more readily formed and more stable than those of nitrogen; compare the unstable $PCl_5$ and the non-existent $NCl_5$, also the stable $P_2O_5$ and

the explosive $N_2O_5$. A comparison of the phosphonium and ammonium salts would appear to point the other way, but the elements are not truly quinquevalent in these compounds.

Between arsenic and antimony a still stronger resemblance is found. Almost every point in the chemistry of the former is parallel in that of the latter, the differences being in general comprised in the fact that antimony and its compounds are more metallic in character than those of arsenic.

There is less resemblance between antimony and bismuth than between arsenic and antimony. Bismuth is very definitely metallic in character, but the existence of its unstable hydride and the volatility and ready hydrolysis of its chloride, etc., make it clear that antimony is the element which resembles it most. The influence of the 'inert pair' of electrons (§ 588) influences the chemistry of bismuth, which hardly ever shows a valency of five.

We see that, though we can trace no resemblance between nitrogen and bismuth, the elements nitrogen, phosphorus, arsenic, antimony, and bismuth form a well-graded series and present a progressive change from typical non-metallic to typical metallic character.

## PHOSPHORUS P, 30·98

**758. History.**—The element phosphorus does not occur free in nature. The name phosphorus was at first loosely applied to more than one 'light bearing' (*φωσφόρος*) substance. Thus the luminous barium sulphide was known as Bologna phosphorus. The element phosphorus was discovered under rather peculiar circumstances in the latter part of the seventeenth century. Brand, of Hamburg, discovered it at a date which is not very certain, probably *c.* 1674; he kept his process secret, but sold it to Krafft, a friend of Kunckel. Boyle and Kunckel from various hints discovered Brand's process independently, and prepared the element by distilling urine, concentrated by evaporation, with sand.

The principle of the method is the same as of the one employed to-day. The evaporated urine furnished the salt, sodium ammonium hydrogen phosphate. This, on heating, furnished sodium metaphosphate, which reacted with silica, furnishing metaphosphoric acid. This reacted with the carbon derived from the organic matter of the urine and gave phosphorus (*cf.* p. 556).

**759. Occurrence.**—Phosphorus is always found in nature in the form of phosphates, the commonest of which is *phosphorite*, tricalcium phosphate $Ca_3(PO_4)_2$. This occurs in North Africa, in parts of the Southern United States, and in many other parts of the world, etc., and is a valuable mineral. Other native phosphates include *coprolite* and *apatite*, $3Ca_3(PO_4)_2.CaCl_2$, found in Canada.

**760. The Phosphorus Cycle in Nature.**—Phosphorus is a necessary constituent of living matter, and is required in small quantities by both animals and plants. The former, of course, derive it ultimately from the latter. All productive soils contain phosphates in small quantities. The phosphorus in the state of nature does not tend to leave the soil as does nitrogen under the influence of denitrifying bacteria. The decay of a plant or animal returns to the soil all the phosphorus it took from it. It is otherwise, however, with cultivated soil. Man grows repeated crops of plants and removes

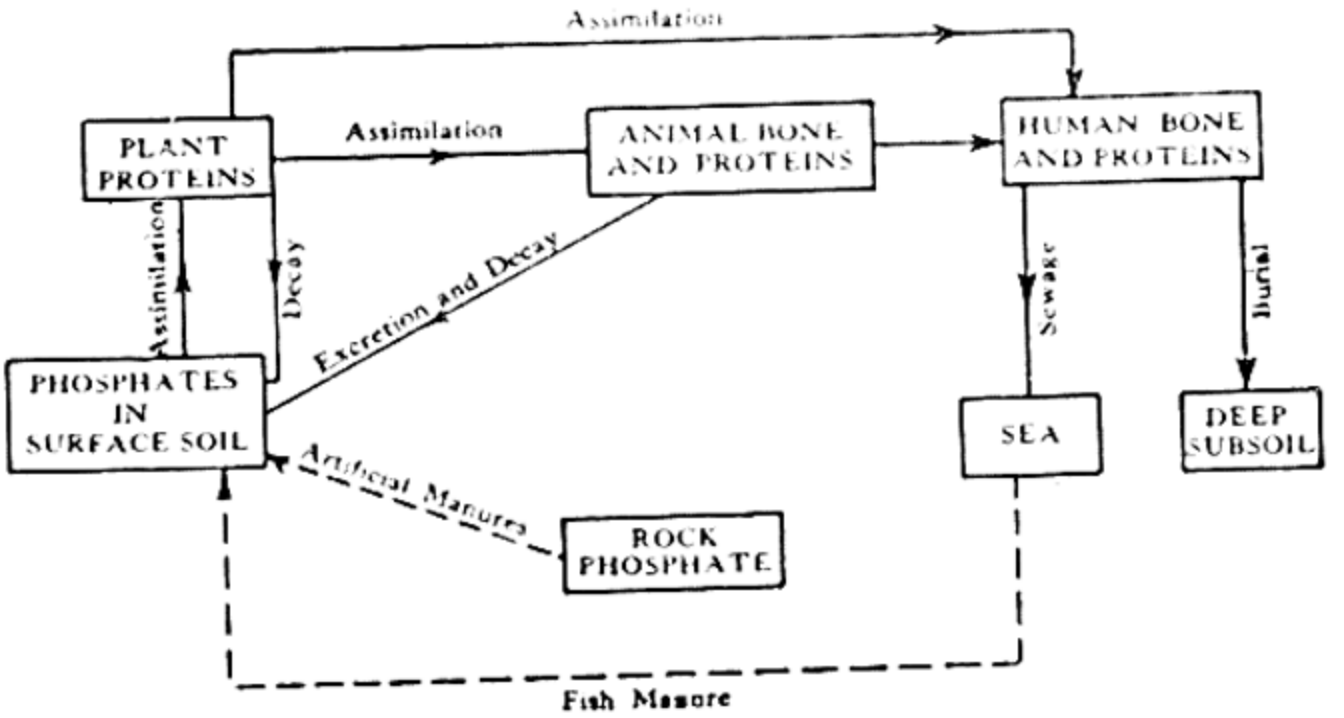


FIG. 142.—Circulation of phosphorus in nature.

them with their phosphorus. All the phosphorus of these crops is run into the rivers with sewage or buried out of reach in cemeteries. It has been found that ordinary soils become deficient in phosphates when repeatedly cropped, and it is now a regular procedure to use phosphates (§ 372) as an artificial manure.

These phosphates are mostly of mineral origin, and until the deposits are exhausted they will maintain our soils in a productive condition. Afterwards, we may hope that science will find some way of dealing with the problem, for otherwise our descendants will be on short rations.

**761. Manufacture.**—Phosphorus is never prepared in the laboratory, but is always purchased either as sticks of white phosphorus packed in tins filled with water, or as red phosphorus, which requires no special precautions in its handling.

White phosphorus is always the form obtained by a chemical preparation and is later, if necessary, converted into the red form.

Phosphorus is made from calcium phosphate. Formerly this was converted into metaphosphoric acid and this distilled with charcoal. This process is now superseded by an electrical method.

*Distillation Process.*—Bones from which the fat has been removed by a solvent or, alternatively, mineral phosphates, are treated with sulphuric acid, thus liberating orthophosphoric acid and precipitating insoluble calcium sulphate. The liquid is filtered off, mixed with charcoal and dried. This latter

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process converts the orthophosphoric acid into metaphosphoric acid. The mixture of metaphosphoric acid and charcoal is heated in fire-clay retorts at a white heat. Phosphorus vapour passes over and is led through iron pipes into troughs of water, where it condenses.

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$
$$H_3PO_4 = H_2O + HPO_3$$
$$2HPO_3 + 6C = H_2 + 6CO + 2P.$$

The modern method of preparing phosphorus employs the electric

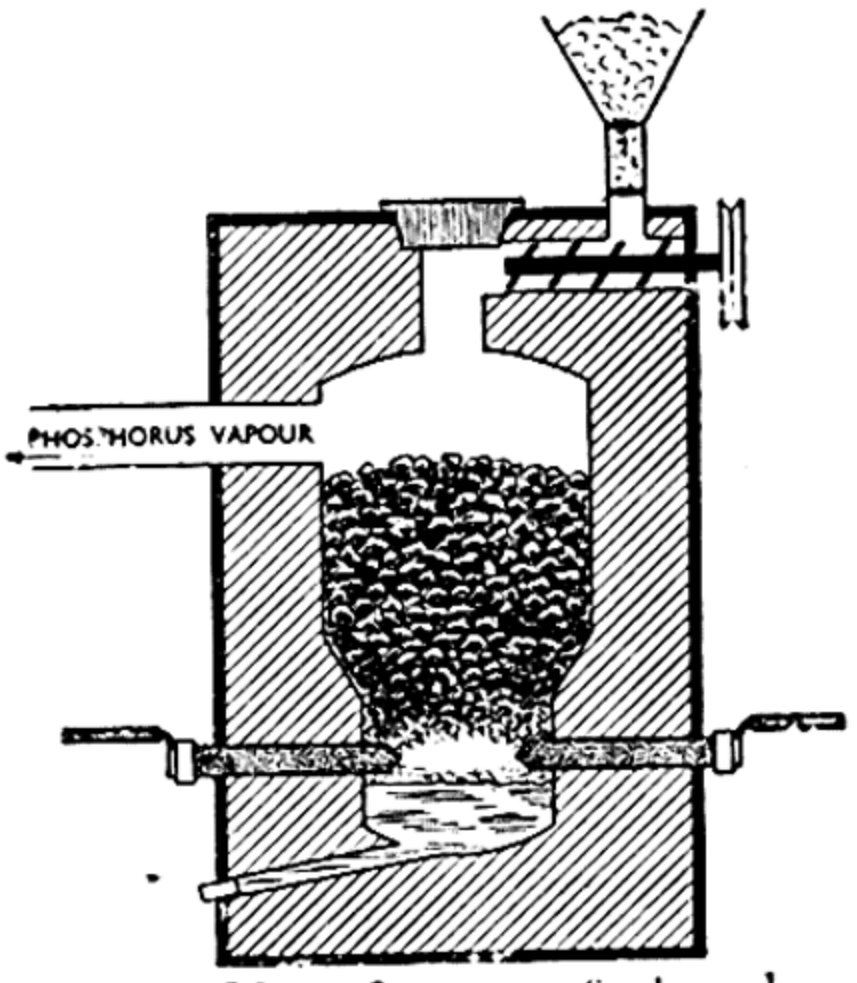



FIG. 143.—Manufacture of phosphorus.

furnace. A charge of sand, coke and calcium phosphate is fed into a furnace of the type illustrated. The current raises the mixture to a white heat when the reaction

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = 6CaSiO_3 + 10CO + P_4$$

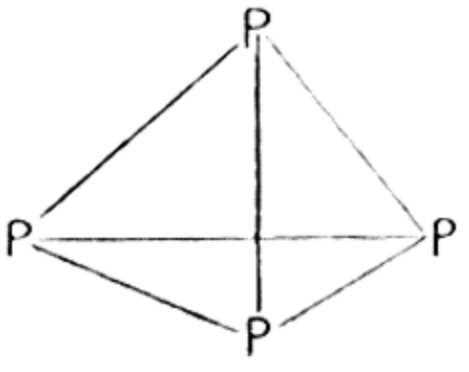
occurs, liberating phosphorus as vapour, while the calcium silicate melts to a slag which is tapped at intervals. The phosphorus vapour is condensed under water.

Phosphorus may, if necessary, be purified by distillation. This operation is best carried out under reduced pressure or in a stream of hydrogen or nitrogen. On the commercial scale white phosphorus is purified by melting it under water and stirring it vigorously. Many other methods have been employed, including the use of oxidising agents, potash, etc.

Commercial red phosphorus which contains traces of white phosphorus (§§ 764, 755), is slowly oxidised when exposed to air and becomes moist as a result of the formation of phosphoric acid. Drying in the air-oven is not safe or satisfactory. The red phosphorus may be stirred with water, allowed to settle, washed again by decantation, sucked moderately dry on a Buchner funnel and dried at a gentle heat in the steam oven.

**762. Formula.**—The vapour density of phosphorus shows that the formula of its vapour is $P_4$. At temperatures above 800° C. there is some dissociation to $P_2$ and P molecules.

X-ray studies indicate that the yellow phosphorus molecule is tetrahedral, thus :—




The structure of red and black phosphorus probably involves a network of such tetrahedra.

**763. Allotropy of Phosphorus.**—Phosphorus exists in two well-marked allotropic forms, white (or yellow) phosphorus and red phosphorus, also incorrectly termed amorphous phosphorus.

Other forms, scarlet, violet and black phosphorus, are known. The first two are apparently identical with red phosphorus in all but the size of their

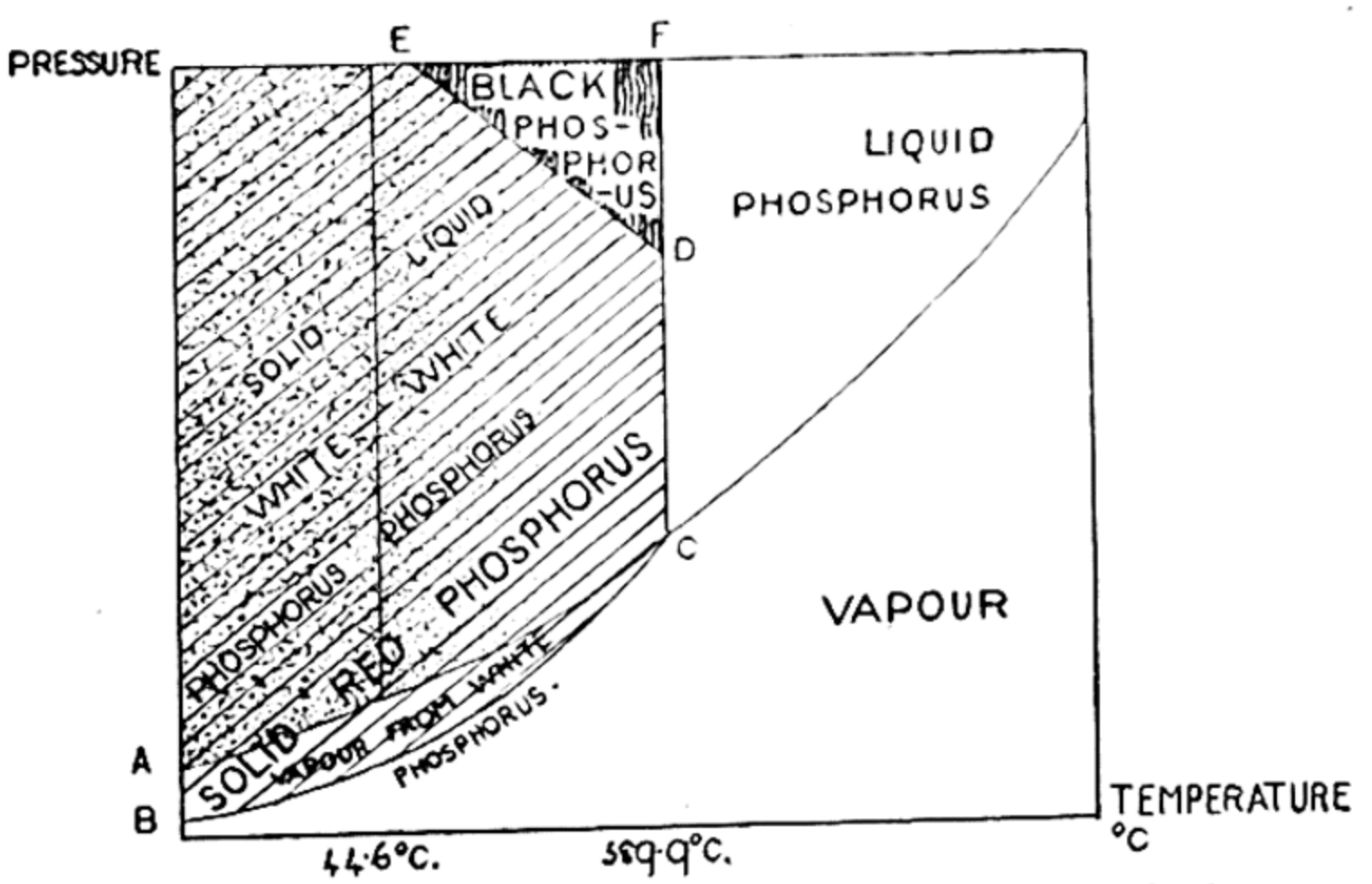



FIG. 144.—Conditions of stability of the allotropic forms of phosphorus.

granules ; black phosphorus, obtained by the action of enormous pressure on heated red phosphorus, may be a distinct form. It resembles red phosphorus in most respects, but is denser and, unlike it, conducts electricity.

White phosphorus is an *unstable* form under all conditions. It has more *energy* than red phosphorus. We find that it has a greater heat of combustion, a lower melting point, a higher vapour pressure, a greater solubility and a much greater chemical reactivity.

If we map out a phase rule diagram for phosphorus it appears much as in Fig. 144. The figure is not to scale, for to show detail the small vapour pressures of the solids have been exaggerated.

It will be seen from the diagram that red phosphorus is the stable solid form at all temperatures, and accordingly it should be found that white phosphorus always changes into the red form. This change does, indeed, take place. At room temperature the change is very slow, but is perceptible as a progressive darkening in colour ; as the temperature rises the change comes more rapid and at about 250° C. the change completes itself in about an hour.

If phosphorus is distilled the product is white phosphorus. The process of condensation is a passing from the condition of vapour to solid or liquid. The vapour has much more energy than the solid or liquid at the same temperature, and so it is found that in almost all cases, including that of phosphorus, the least stable form of the solid is formed by condensation. The least stable form is that with most energy and is therefore that formed from the vapour by the least energy-change.

**764. Manufacture of Red Phosphorus.**—Red phosphorus is made by heating white phosphorus in absence of air to 240–260° C., at which temperature it rapidly assumes the more stable form, liberating energy in so doing. The white phosphorus is heated in an iron pot provided with an open narrow tube inserted in its cover. This tube provides for the release of any pressure. The air in the pot is soon used up by the heated phosphorus and thereafter but little enters by the vent tube. Too high a temperature must not be used lest the rapid conversion of white phosphorus into the red variety might liberate heat so rapidly as to cause a dangerous explosion. The red phosphorus is ground under water and freed from white phosphorus by boiling with caustic soda, which attacks the latter (p. 556), but not the former.

**765. Physical Properties of Red and White Phosphorus.**—These are perhaps best expressed and compared in tabular form.

| | Red Phosphorus. | White Phosphorus. |
|---|---|---|
| M.P. . . . | 600–615° C.[1] | 43·3° C. |
| B.P. . . . | Very high | 290° C. |
| Density . . . | 2·16 | 1·836 |
| Solubility in water . | Insoluble | Very slightly soluble. |
| Solubility in other solvents. | Insoluble in all solvents | Soluble in carbon disulphide, turpentine, alcohol, oils, etc. |

[1] The purer form, ' violet ' phosphorus, melts at 589·9° C.

**766. Physiological Effect.**—Red phosphorus is inert when taken into the system. It is insoluble and non-volatile and passes through

the body unchanged. White phosphorus, on the other hand, is one of the most poisonous substances in existence, 0·04 gms. having formed a fatal dose. It finds a use as a rat poison, for its garlic-like odour and taste are apparently attractive to rats. It is said, indeed, that in the nineteenth century, when white phosphorus was used in matches, rats caused serious fires by gnawing the heads and igniting the whole box.

Even the vapour of phosphorus is poisonous. Workers with white phosphorus suffer from decay of the teeth and finally of the whole jaw-bone. The danger of the continual handling of phosphorus has led to the prohibition by every civilised country of the use of white phosphorus in matches.

**767. Chemical Properties of Phosphorus.**—Both red and white phosphorus are highly reactive substances, but more especially the latter.

Both forms of phosphorus burn in air or oxygen, forming the pentoxide together with some trioxide,

$$4P + 5O_2 = P_4O_{10}$$
$$4P + 3O_2 = 2P_2O_3.$$

White phosphorus differs from red phosphorus in that it combines with oxygen at room temperature, phosphorus trioxide being the main product. In doing this phosphorus gives out a peculiar glow, which has been the subject of much study.

The glow of phosphorus resembles a flame in that it consists of a combustible vapour in the act of combination with oxygen. Thus the glow may be detached and made to move by the action of a current of air. But it differs from the ordinary flame in that it is cold or nearly so. Cold flames are not altogether unknown. The hand can be held in the flame of thiophosphoryl fluoride $PSF_3$ without being burnt. The light given out arises from the chemical energy of the reaction, not from the glowing of a hot gas.

The glow of phosphorus exhibits several peculiar features. In the first place, no glow takes place if the partial pressure of oxygen is below or above a certain value. Thus phosphorus does not glow in pure oxygen at atmospheric pressure nor in oxygen at less than 1 mm. pressure. At intermediate pressures (1-600 mm.) glowing takes place. The process is probably a chain reaction.

A $P_2$ molecule is thought to react with oxygen, forming a phosphorus oxide molecule in an activated condition. The energy of this activated [1] molecule decomposes a $P_4$ molecule to two $P_2$ molecules, which again react, setting up a chain of chemical reaction.

(1) $P_4 \rightarrow 2P_2$.

(2) $P_2$ + oxygen → phosphorous oxide* + radiation.

(3) $P_4$ + phosphorous oxide* → $2P_2$ + phosphorous oxide.

At very low pressures the chains propagate in a linear manner and the reaction is too slow for the glow to be noticeable. At intermediate pressures

[1] See § 583 (1), also note, p. 249.

more chains start in a given time than are broken by reaching the walls of the vessel (or the limits of the space containing the phosphorus vapour). The reaction is thus much accelerated. At higher pressures the oxygen molecules are in great excess and their collisions with any molecule are so much more frequent than any others that stage (3) does not readily take place, and the chains are broken at an early stage and the reaction practically ceases.

This view of the reaction accounts for the fact that traces of the vapour of many substances extinguish the glow. Thus a trace of turpentine vapour does so. It is supposed that the molecules of these substances take up the energy from the activated molecules and so break the chains. Ozone is produced during the oxidation. It is thought that its production is due to the effect of the very short waves of the light of the glow on the oxygen present.

White phosphorus is much more inflammable than red phosphorus. While the latter catches fire at about 260° C., white phosphorus ignites at 30–40° C. Since the temperature of the body is about 37° C. the handling of white phosphorus may inflame it. If this occurs the phosphorus sticks to the flesh and is difficult to remove, causing a painful and intractable burn. It is, therefore, always advisable to handle white phosphorus with tongs. White phosphorus, in a finely-divided state, may oxidise rapidly enough to catch alight. Thus, if a strong solution of phosphorus in carbon disulphide is allowed to evaporate, the film of phosphorus so formed will often burst into flames. White phosphorus is always stored under water, and it should not be cut into pieces unless it is immersed in cold water.

Phosphorus reacts with the halogens, white phosphorus more readily than the red form. In all cases the trihalide is formed first, and on further treatment with halogen the pentahalide [1] is produced.

$$2P + 3Cl_2 = 2PCl_3$$
$$PCl_3 + Cl_2 = PCl_5.$$

Phosphorus reacts with sulphur and forms various compounds of which the sulphides, $P_4S_3$ and $P_2S_5$, are the best known. The first is used as a combustible in the match industry.

Phosphorus reacts with most of the metals, forming phosphides. Thus, if a piece of sodium, as large as a pea, be cautiously heated in a closed crucible, with a piece of *dry* phosphorus of the same size, they combine with a bright flash, forming sodium phosphide $Na_3P$. This when immersed in water gives spontaneously inflammable phosphine (*q.v.*).

Phosphorus is a powerful reducing agent, more especially the white form. Strong oxidising agents, such as nitric acid, convert it readily into orthophosphoric acid (*q.v.*).

White phosphorus, but not the red form, will reduce the salts of the noble metals and also of copper to the metallic state. If a piece

[1] The existence of the pentaiodide, $PI_5$, is not very certain.

of phosphorus be immersed in copper sulphate solution it becomes coated with black copper phosphide and some metallic copper.

$$4P + 3CuSO_4 + 6H_2O = Cu_3P_2 + 2H_3PO_3 + 3H_2SO_4$$
$$Cu_3P_2 + 5CuSO_4 + 8H_2O = 8Cu + 5H_2SO_4 + 2H_3PO_4$$

White phosphorus reacts with caustic soda to form hydrogen and phosphine (*q.v.*), while red phosphorus is unaffected,

$$4P + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3.$$

This property is used to remove traces of white phosphorus from the red variety.

**768. Uses of Phosphorus.**—The main use of phosphorus is in the match industry. White phosphorus is no longer permitted to be used in matches, but red phosphorus or a sulphide of phosphorus is always employed. A match-head of the strike-anywhere variety may contain tetraphosphorus trisulphide together with potassium chlorate, manganese dioxide or other oxidising compounds. These are mixed with a binding material, such as gum or glue and some inert substance, such as chalk or powdered glass, to reduce the sensitiveness of the mixture. When the match is struck the local heat of friction ignites the combustible mass.

Safety matches contain the same types of ingredient but have no phosphorus in the heads, which therefore are difficult to ignite. The boxes are coated with a mixture of red phosphorus and powdered glass, etc. The phosphorus ignites locally when the match is struck and sets fire to the combustibles of the head.

Some phosphorus is used in making phosphorus trichloride and pentachloride, which have uses in the chemical industry. White phosphorus is used in medicine and in rat poisons. It finds occasional uses in fireworks and in incendiary bombs, smoke bombs, etc.

Phosphorus is added to bronze in order to make the extremely strong and tough alloy, phosphor-bronze. This contains scarcely any phosphorus, and it is thought that the phosphorus acts by removing the oxygen of the cuprous oxide, which is usually contained in bronze, being formed when the alloy is melted in air.

**769. Atomic Weight of Phosphorus.**—The atomic weight is approximately 31, for none of its volatile compounds, *e.g.*, phosphine, phosphorus trioxide, trichloride, tribromide, etc., contain less than 31 gms. of phosphorus per gram-molecule. The value 31, moreover, finds a suitable place and valency for the element in the periodic table. The exact atomic weight has, amongst other methods, been calculated from the weight of silver bromide, made from a given weight of silver phosphate (the atomic weights of silver and bromine being accurately known and that of oxygen being the standard). Another value was obtained from an accurate determination of

the density of phosphine. G. Ter-Gazarian prepared the gas by the action of water on calcium phosphide, purified it by repeated liquefaction and fractional distillation and weighed it in a glass 'balloon.' He found that 1 litre of the gas weighed 1·5293 gms. This gives a molecular weight of 33·930, and taking hydrogen as 1·008, a value of 33·930 — 3·024 = 30·906. The value adopted by the Committee on atomic weights is 30·98.

## Phosphorus Hydrides.

**770. Phosphine $PH_3$.**—The hydrides of phosphorus show little resemblance to those of nitrogen. Phosphine is, it is true, slightly basic and forms salts, such as phosphonium iodide $PH_4I$. None the less, in consequence of its *instability* and its considerable *reducing* power, phosphine has little likeness to ammonia.

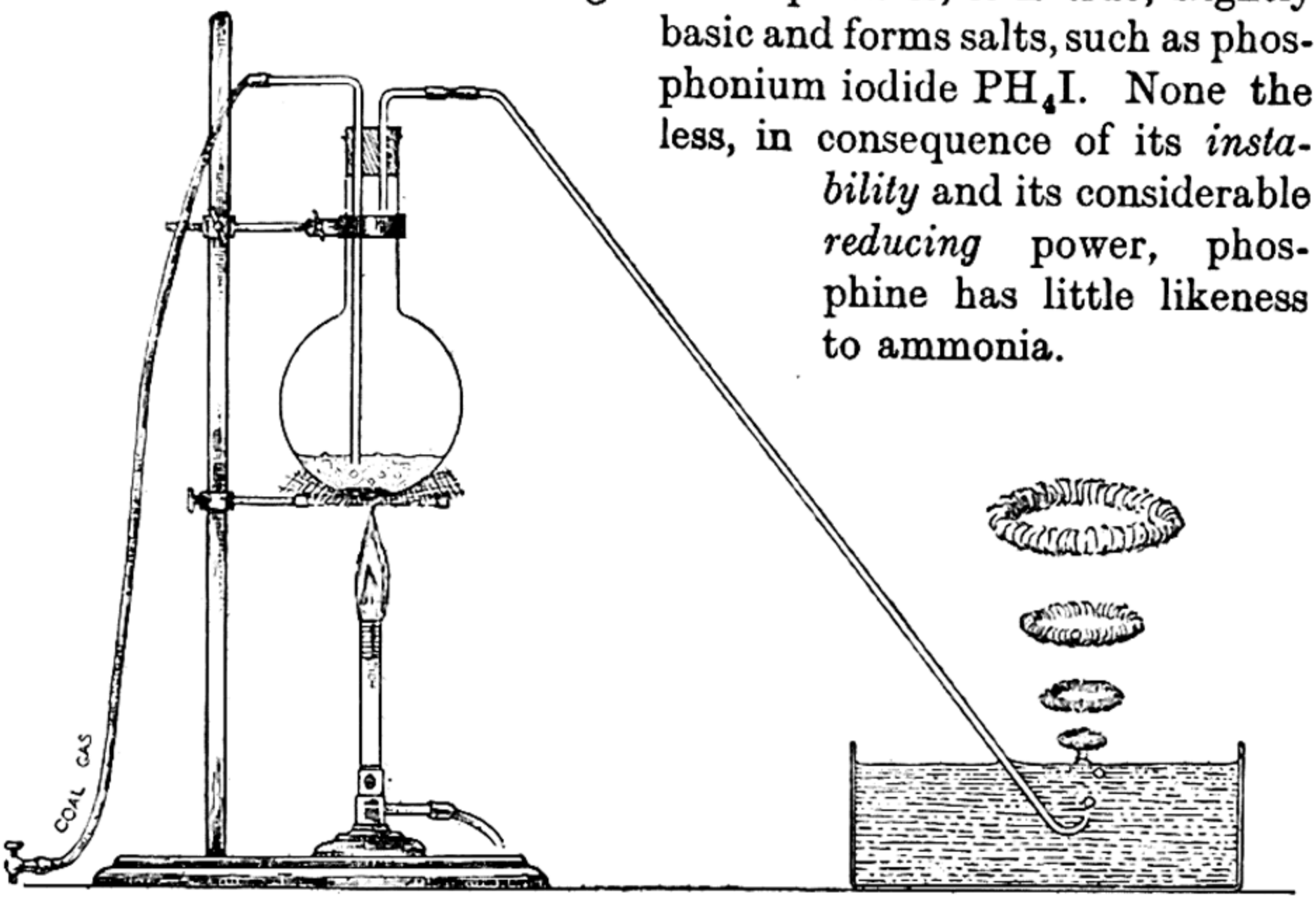



Fig. 145.—Preparation and combustion of phosphine.

*Preparation.*—Phosphine is probably formed when organic matter decays, and the faint luminosity occasionally seen over marshes and churchyards, and feared by our forefathers as "will-o'-the-wisps" or "corpse-candles," is sometimes thought to be due to the oxidation of phosphine. It is very doubtful if enough phosphine to cause such a phenomenon is ever produced by decay.

Phosphine is best prepared by the action of sodium hydroxide on white phosphorus. Sodium hypophosphite and phosphine are formed.[1]

$$3NaOH + 4P + 3H_2O = 3NaH_2PO_2 + PH_3.$$

[1] It is interesting to compare the analogous action of caustic soda on other elements. In every case where any action takes place the sodium salt of an acid containing the oxygen and the element is formed together with hydrogen or the hydride of the element or a salt derived from the action of the hydride on caustic soda (see the cases of aluminium, zinc, silicon, sulphur, chlorine).

It is necessary to ensure the absence of air throughout the experiment, for phosphine, as produced by this process, is spontaneously inflammable. The apparatus figured above may be used. Five grams of white phosphorus are placed in the flask together with 100 c.c. of a strong solution of caustic soda (20 per cent.). Air is then displaced from the apparatus by a stream of coal-gas. The mixture is heated and phosphine is evolved. Each bubble of the gas ignites as it leaves the water and produces beautiful and characteristic vortex rings of phosphorus pentoxide smoke. The gas is very poisonous, and even in small quantities may cause unpleasant headaches. It is best, therefore, to perform the experiment at a time when the laboratory can be left empty for an hour or so.

Phosphine can also be made by the action of water on certain metallic phosphides, notably those of sodium or calcium. A piece of *dry* phosphorus, the size of a pea, may be warmed in a closed crucible with a similar piece of sodium ; the elements combine with vigour. The crucible containing the phosphide is then immersed in a trough of water, when bubbles of phosphine are at once evolved and burn at the surface of the water.

$$Na_3P + 3H_2O = 3NaOH + PH_3.$$

Calcium phosphide has been employed for signal-flares to be used at sea. These consist of a float bearing a vessel containing calcium phosphide. When dropped into the sea they evolve spontaneously inflammable phosphine, which cannot be extinguished by sea water, rain, etc.

*Formula of Phosphine.*—The formula of phosphine may be obtained by heating it with copper by electric sparks, when copper phosphide, red phosphorus, and hydrogen are formed. Two volumes of phosphine give three volumes of hydrogen showing the formula to be $P_nH_3$,

$$\underset{\text{2 vols.}}{2P_nH_3} = 2nP + \underset{\text{3 vols.}}{3H_2}.$$

That $n = 1$ is shown by its density of 17, which corresponds to the formula $PH_3$.

*Properties.*—Phosphine is a colourless gas with a strong fishy or garlic-like odour. It is poisonous when breathed. The gas has a density of 17 ($H_2 = 1$) and is slightly soluble in water. It can be liquefied (B.P. — 85° C.) ; the liquid solidifies at — 133° C.

Phosphine, when pure, is not spontaneously inflammable. If the gas, obtained as described above, is passed through a long spiral tube cooled in a freezing mixture of ice and salt, a liquid condenses and the gas passing on no longer ignites when brought into the air. The condensed liquid is the hydride $P_2H_4$, described below, and it is

the presence of this impurity that renders phosphine spontaneously inflammable. Phosphine burns in air, forming phosphorus pentoxide and water,

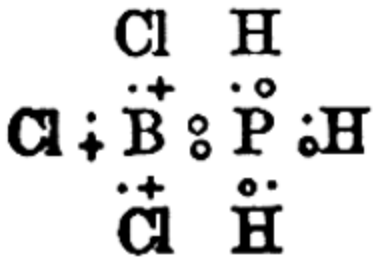
$$4PH_3 + 8O_2 = P_4O_{10} + 6H_2O.$$

Phosphine is a powerful reducing agent. When passed into solutions of copper salts, a red precipitate of copper or copper phosphide results. With silver and gold salts reduction to the metal takes place.

Phosphine $PH_3$ resembles ammonia $NH_3$, in having some basic properties. When phosphine and a hydrogen halide are mixed a *phosphonium* salt is produced,

$$PH_3 + HBr = PH_4Br.$$

It can also form some co-ordinate compounds like those of ammonia, *e.g.*, the compound, $BCl_3 \leftarrow PH_3$, which we may represent as



distinguishing the electrons from the phosphorus atom by the sign o and those from the boron atom by the sign +.

Phosphine may be detected by its odour and its action upon copper or silver salts. The action of the gas on copper salts might cause it to be mistaken for acetylene ; phosphine, however, reduces these salts in *acid* solution, while the red cuprous acetylide is not formed except in neutral or alkaline solution.

**771. Phosphonium Iodide** is the best-known phosphonium salt. It is best made by dissolving phosphorus and iodine in carbon disulphide. The carbon disulphide is then distilled off and the calculated quantity of water is added drop by drop to the mixture contained in a retort. The phosphonium iodide is sublimed over in a stream of dry carbon dioxide,

$$5I + 9P + 16H_2O = 5PH_4I + 4H_3PO_4.$$

Phosphonium iodide is a beautifully crystalline colourless salt, which volatilises even at room temperature. It decomposes into phosphine and hydrogen iodide when heated above 30° C., and when mixed with water it forms the same products. It finds some uses in organic chemistry.

**772. Phosphorus Dihydride $P_2H_4$** is separated from phosphine as described above. The action of hot water on calcium phosphide yields a gas particularly rich in this compound. It is a colourless liquid, spontaneously inflammable in air. It decomposes on standing, yielding the solid hydride together with phosphine.

A yellow solid, said to be *Phosphorus hydride* $P_{12}H_6$, is also produced in the above reaction. It is decomposed by heat into phosphine and phosphorus.

Several other solid hydrides have been described.

## Oxides of Phosphorus

**773. The Oxides of Phosphorus.**—The oxides of phosphorus include :—

| | |
|---|---|
| Phosphorous oxide, phosphorus trioxide . | $P_4O_6$ |
| Phosphorus tetroxide . . . . | $P_2O_4$ |
| Phosphorus pentoxide . . . . | $P_4O_{10}$ |
| Phosphorus peroxide . . . . | $P_2O_6$ |

**774. Phosphorous Oxide $P_4O_6$** results when phosphorus oxidises slowly in air. White phosphorus in the tube A is gently heated in a current of air.

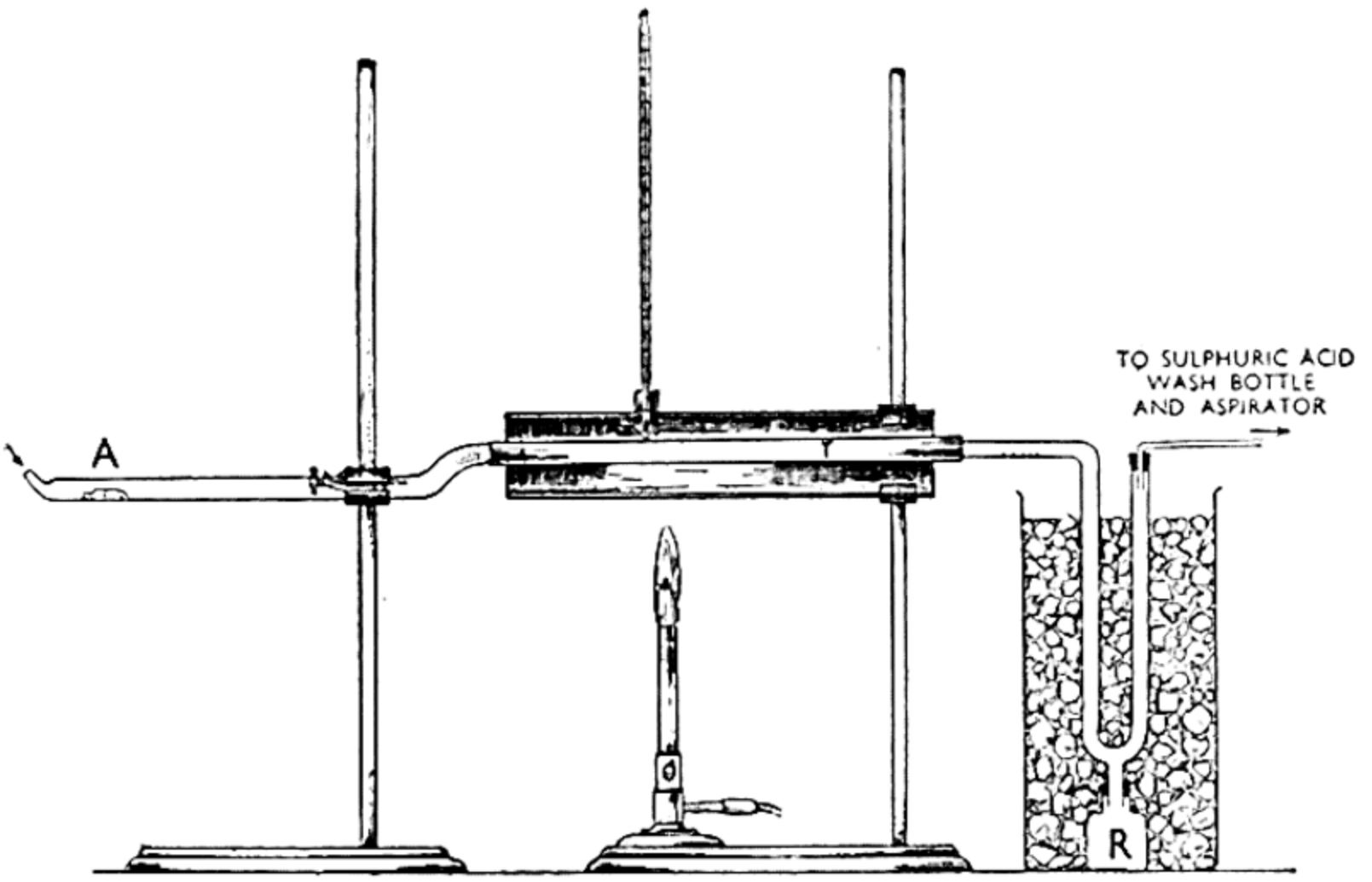



FIG. 146.—Preparation of phosphorus trioxide.

A mixture of the trioxide and pentoxide is formed, and these condense in the brass tube T, which is cooled by a water jacket. The water jacket is then warmed up to 50–60° C., when the volatile trioxide is carried over and is condensed in the cooled U-tube as a white waxy solid, which, on replacing the freezing mixture by warm water, melts and runs into the receiver R.

Phosphorus trioxide is a white waxy volatile solid of garlic-like odour. When gently heated in air it burns with great brilliancy, forming the pentoxide,

$$P_4O_6 + 2O_2 = P_4O_{10}.$$

With water phosphorous acid is formed,

$$P_4O_6 + 6H_2O = 4H_3PO_3.$$

**775. Phosphorus Tetroxide $P_2O_4$** has been obtained by subliming the mixture of oxides obtained by the slow combustion of phosphorus. It forms colourless transparent crystals, which dissolve in water, giving phosphorous and phosphoric acids, therein showing a resemblance to nitrogen tetroxide (§ 723),

$$P_2O_4 + 3H_2O = H_3PO_4 + H_3PO_3.$$

**776. Phosphorus Pentoxide $P_4O_{10}$.**—Phosphorus pentoxide, the most important oxide of phosphorus, results when the element is burned in an ample supply of air.

$$P_4 + 5O_2 = P_4O_{10}.$$

The phosphorus may be burned in an iron dish suspended in a large glass globe, which is supplied with well-dried air. Fresh phosphorus is added from time to time, and the pentoxide falls directly into the bottle in which it is to be stored. It is best purified by heating it to 600–700° C. in an iron tube, through which a brisk current of oxygen passes. The pentoxide vapour is carried on into a glass tube attached to the iron tube and there condenses. The oxygen oxidises any lower oxides to the pentoxide. The action of ozonised air on the oxide heated to 175–220° C. also removes these oxides.

Phosphorus pentoxide is a white solid. When heated it vaporises at a red heat and the density of the vapour indicates the formula $P_4O_{10}$. The formula $P_2O_5$, however, describes its chemical reactions equally well, and is commonly used.

Phosphorus pentoxide is an acidic oxide. It reacts very vigorously with water, hissing and giving out much heat. With cold water metaphosphoric acid is formed, and with hot water orthophosphoric acid,

$$P_2O_5 + H_2O = 2HPO_3$$
$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

Its property of combining with water and forming the non-volatile metaphosphoric acid renders it most useful for removing the last traces of moisture from a gas already partially dried. Phosphorus pentoxide is, however, useless for removing *large* quantities of moisture, for it soon becomes covered with a gelatinous skin of metaphosphoric acid, which screens the unused pentoxide from further action. The remarkable experiments on intensive drying (§§ 205, *seq.*) have all been carried out by means of phosphorus pentoxide. Other drying agents, sulphuric acid, calcium chloride, etc., as soon as they have absorbed a little water, evolve traces of water vapour, and so cannot dry a gas completely. Phosphorus pentoxide forms a completely stable compound with the water and cannot release it once it has been absorbed.

Phosphorus pentoxide will not only absorb free water but will decompose many compounds in such a way as to produce water, with which it then combines.

Thus with sulphuric and nitric acids it forms the anhydrides, sulphur trioxide and nitrogen pentoxide respectively.

$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3$$
$$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5.$$

With oxamide it forms cyanogen,

$$\begin{matrix}CO.NH_2\\|\\CO.NH_2\end{matrix} + 2P_2O_5 = \begin{matrix}CN\\|\\CN\end{matrix} + 4HPO_3.$$

**776a. Phosphorus peroxide $P_2O_6$** is obtained when a mixture of the

pentoxide and oxygen are passed through a hot discharge tube. It is a bluish-violet solid, which with water gives a per-acid, probably $H_4P_2O_8$.

**777. The Acids of Phosphorus and their Structure.**—The most definite acids of phosphorus are :—

| | |
|---|---|
| Hypophosphorous acid . . | $H_3PO_2$ |
| Phosphorous acid . . . | $H_3PO_3$ |
| Hypophosphoric acid . . | $H_4P_2O_6$ |
| Orthophosphoric acid . . | $H_3PO_4$ |
| Pyrophosphoric acid . . | $H_4P_2O_7$ |
| Metaphosphoric acid . . | $HPO_3$ |
| Perphosphoric acids . . | $H_3PO_5$ and $H_4P_2O_8$ |

The structures of these acids can only be made clear by considering their electronic structure.

*Hypophosphorous acid* $H_3PO_2$ is actually monobasic, forming salts of the formula $M'H_2PO_2$ only. The formula must therefore be $H[H_2PO_2]$.

*Phosphorous acid* $H_3PO_3$ is actually dibasic, and is to be regarded as $H_2[HPO_3]$.

*Orthophosphoric acid* $H_3PO_4$ is tribasic and is to be regarded as $H_3[PO_4]$.

Considering these from the point of view of the electronic theory of valency these facts are easily explained. The phosphorus atom has an outer ring of five electrons, $:\ddot{P}\cdot$ It may make up its ring to eight by forming three covalent linkages or by receiving electrons, so forming a part of a negatively charged ion. In either case there will be one or more unshared pairs of electrons which may be given to other atoms by *co-ordinate* linkage. The following formulæ show clearly the structure and behaviour of the compounds of phosphorus with four other atoms.

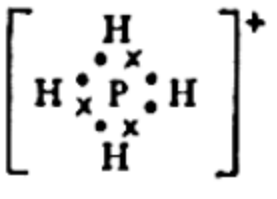
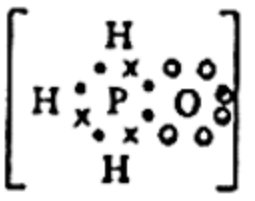
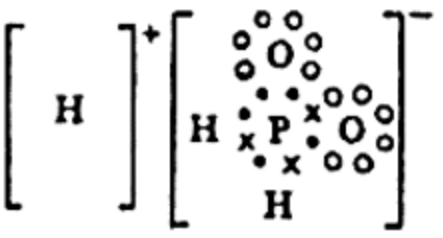
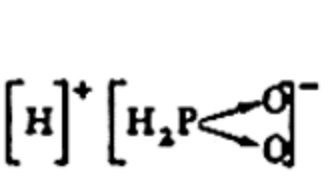
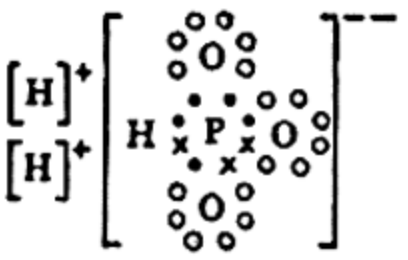
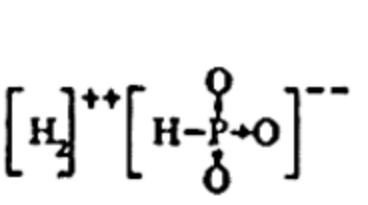
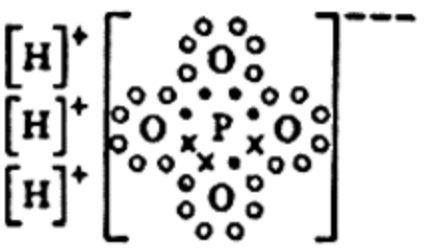
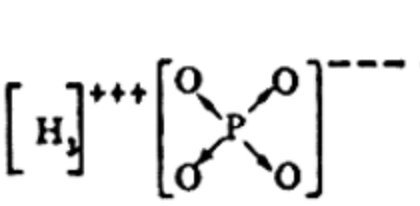
| | | | |
|---|---|---|---|
| Phosphonium ion. |  | $H_3P\rightarrow H$ | Positively charged. |
| Hypothetical oxy-phosphine. |  | $H_3P\rightarrow O$ | Neutral. |
| Hypophosphorous acid. |  |  | Monobasic negative ion formed. |
| Phosphorous acid. |  |  | Dibasic negative ion formed. |
| Orthophosphoric acid. |  |  | Tribasic negative ion formed. |

FIG. 147

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In the group $[PO_nH_{4-n}]$ the replacement of a hydrogen atom (which supplies an electron) by an oxygen atom (which does not, being co-ordinated to the phosphorus by *receiving* two electrons), necessitates the taking in of a single electron by the group. Thus the substitution of a hydrogen atom by an oxygen atom increases the negative charge of the ion and therefore the basicity of the acid by one unit. We see also how it is that all the hydrogen atoms of phosphorous and hypophosphorous acids are not replaceable.

The structures of the remaining acids of phosphorus are the following:

*Pyrophosphoric Acid.*—The seven oxygen atoms had originally 42 electrons, and the two phosphorus atoms 10, 52 in all. The above formula contains 56.

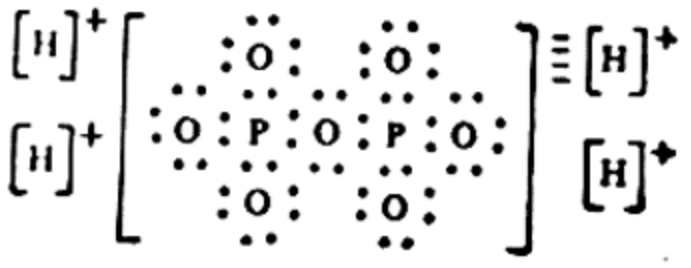


FIG. 148.—Pyrophosphoric acid.

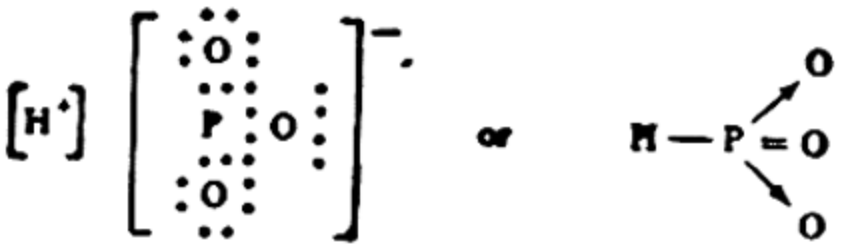


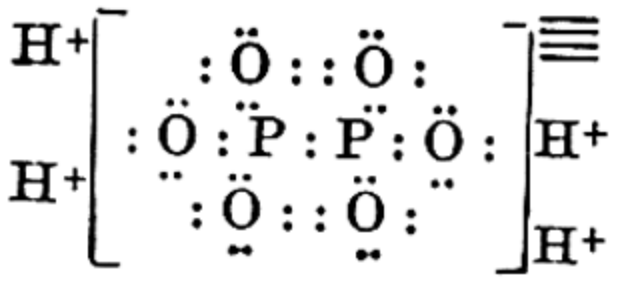
FIG. 149.—Metaphosphoric acid.

Four have been taken from outside and the charge of the group (the basicity of the acid) is $56 - 52 = 4$.

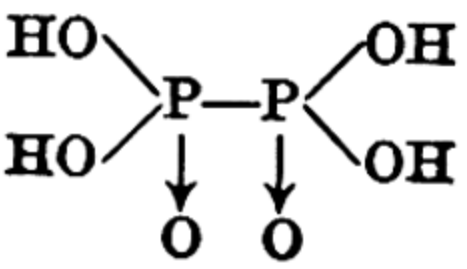
*Metaphosphoric Acid.*—The $PO_3$ group is monobasic, for it contains twenty-four valency electrons, while its constituent atoms originally contained twenty-three.

*Hypophosphoric Acid* $H_4P_2O_6$.—The formula of this acid was formerly considered to be $H_2PO_3$, in which case the phosphorus atom would have had a septet of electrons.

Recent work has shown that the ethyl ester is $(C_2H_5)_4P_2O_6$, and not as formerly believed $(C_2H_5)_2PO_3$. Its structure is accordingly in the dissociated form,



and in the undissociated form



**778. Hypophosphorous Acid $H_3PO_2$.**—When white phosphorus is boiled with alkalis (§ 770) hypophosphites are formed. If barium hydroxide is the alkali employed barium hypophosphite results. This may be treated

$$3Ba(OH)_2 + 8P + 6H_2O = 2PH_3 + 3Ba(H_2PO_2)_2$$

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2H_3PO_2,$$

with the exact quantity of sulphuric acid needed to precipitate the barium. The barium sulphate is filtered off and the clear solution concentrated till it crystallises on cooling.

Hypophosphorous acid is a crystalline solid. It is a monobasic acid, only one of its hydrogen atoms being replaceable by those of a metal. Its structure is discussed in § 777. Both the acid and its salts are very powerful reducing agents. Thus a solution of a hypophosphite will reduce copper sulphate not only to copper but even to the red copper hydride (probably $CuH_2$).

$$H_3PO_2 + 2H_2O + CuSO_4 = H_3PO_4 + H_2SO_4 + CuH_2.$$

**779. Phosphorous Acid.**—Phosphorous acid may be prepared by the action of phosphorus trioxide on water.

$$P_2O_3 + 3H_2O = 2H_3PO_3,$$

or more readily by the action of phosphorus trichloride on water. The hydrochloric acid formed may be removed by cautious distillation,

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

Phosphorous acid is a solid which melts at 70·1° C. When heated it decomposes, forming orthophosphoric acid and phosphine,

$$4H_3PO_3 = PH_3 + 3H_3PO_4.$$

Oxidising agents readily convert phosphorous acid into orthophosphoric acid,

$$2HNO_3 + H_3PO_3 = H_2O + 2NO_2 + H_3PO_4.$$

The phosphites and phosphorous acid are therefore very powerful reducing agents, reducing salts of copper, gold, silver, etc., to the metals.

**780. Hypophosphoric Acid $H_2PO_3$.**—The structure of this compound has already been discussed. The acid is prepared together with phosphoric and phosphorous acid by the action of moist air on phosphorus.

The acid forms crystals, melting at 70° C. In presence of acids it hydrolyses, forming phosphorous and phosphoric acids,

$$2H_2PO_3 + H_2O = H_3PO_3 + H_3PO_4.$$

It is a mild reducing agent.

## Phosphoric Acids

**781. The Phosphoric Acids.**—Three acids are derived from phosphorus pentoxide :—

| | |
|---|---|
| Orthophosphoric acid . . . | $H_3PO_4$ |
| Pyrophosphoric acid . . . | $H_4P_2O_7$ |
| Metaphosphoric acid . . . | $HPO_3$ |

All three may be regarded as derived from phosphorus pentoxide, but as they cannot, of course, be regarded as containing in their structure either water or phosphorus pentoxide, their formulæ should only be written

$$P_2O_5 . 3H_2O, \quad P_2O_5 . 2H_2O, \quad P_2O_5 . H_2O$$

as a reminder of their derivation, not as an indication of their structure.

The structure of these acids has already been fully discussed.

**782. Orthophosphoric acid** may be prepared by the action of water on phosphorus pentoxide. The latter is added cautiously to distilled water, and the resulting solution is boiled to convert any metaphosphoric acid into orthophosphoric acid,

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

More usual methods of preparation are by the oxidation of phosphorus or from calcium phosphate.

The former method is the usual laboratory one. Ten gms. of red phosphorus are placed in a 2-litre flask together with 300 c.c. of nitric acid (sp. gr. 1·2 [1]). A crystal of iodine is added and the mixture is heated on a water bath in a good fume cupboard. Great quantities of nitrogen tetroxide and nitric oxide are evolved. The

[1] Equal volumes of water and ordinary concentrated acid (sp. gr. 1·4). Stronger acid may cause an explosion.

solution of orthophosphoric acid is evaporated until no more acid fumes are evolved, the temperature being kept below 180° to prevent decomposition.

The trace of iodine probably acts by forming phosphorus iodide, which reacts with water to hydrogen iodide and phosphorous acid. These are oxidised by nitric acid, the first forming iodine once more and the latter orthophosphoric acid,

$$P + 3I = PI_3$$
$$PI_3 + 3H_2O = H_3PO_3 + 3HI$$
$$3HI + 3HNO_3 = 3H_2O + 3NO_2 + 3I$$
$$\underline{H_3PO_3 + 2HNO_3 = H_3PO_4 + H_2O + 2NO_2}$$
$$P + 5HNO_3 = H_3PO_4 + 5NO_2 + H_2O.$$

A commercial method of making the acid by the action of sulphuric acid on calcium phosphate is mentioned on p. 555 under the preparation of phosphorus.

Orthophosphoric acid, as usually met with, is a colourless syrupy liquid which if free from water solidifies to a mass of crystals melting at 38·6° C. It is not volatile at the ordinary temperature and is freely miscible with water in all proportions.

When heated it decomposes, pyrophosphoric acid being first formed at about 250° C.,

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

Further heating produces metaphosphoric acid,

$$H_3PO_4 = HPO_3 + H_2O.$$

Orthophosphoric acid has normal acidic properties. It is a tribasic acid and ionises to form three negative ions,

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \rightleftharpoons 2H^+ + HPO_4^{--} \rightleftharpoons 3H^+ + PO_4^{---}$$

$H_3PO_4$ behaves like a moderately strong acid, $H_2PO_4^-$ like a weak acid such as acetic acid, and $HPO_4^{--}$ like a very weak acid such as hydrocyanic acid or phenol. Thus, when phosphoric acid is titrated with caustic soda solution, using methyl orange as indicator, the colour change takes place when all the $H_3PO_4$ has been converted into $H_2PO_4^-$ (when $NaH_2PO_4$ has been formed), for the latter ion is a weaker acid than methyl orange. If phenolphthalein is used for the titration we find that the colour change takes place when $H_2PO_4^-$ has been all converted into $HPO_4^{--}$, for $H_2PO_4^-$ is a stronger acid than phenolphthalein. No indicator will show the complete conversion of $HPO_4^{--}$ into $PO_4^{---}$.

Orthophosphoric acid forms three sodium salts,

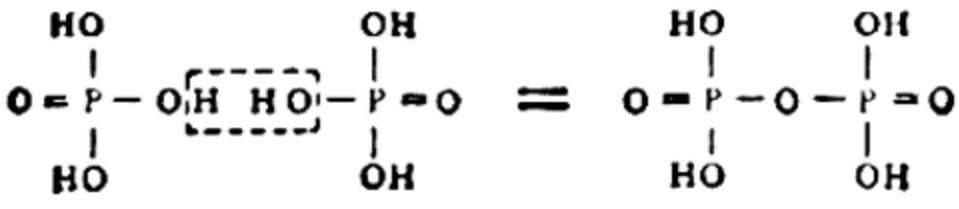
$$NaH_2PO_4 . (H_2O),\ Na_2HPO_4 . (12H_2O),\ Na_3PO_4(12H_2O).$$

Solutions of the first salt are weakly acid in reaction, those of the second are weakly alkaline, and those of the third strongly alkaline. The reason why an *acid* salt may react *alkaline* is explained in § 121.

Phosphoric acid finds certain uses in chemical practice as a substitute for sulphuric acid, where the oxidising properties of the latter cause inconvenience. Thus hydrobromic acid may be made by the action of phosphoric acid on potassium bromide, where sulphuric acid would give a product mixed with bromine and sulphur dioxide (§ 1078).

The phosphates are discussed under the headings of the various metals.

**783. Pyrophosphoric Acid $H_4P_2O_7$.**—Pyrophosphoric acid is made by heating orthophosphoric acid to 215° C. for some time.



$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

Pyrophosphoric acid is a solid of low melting point. It is a tetrabasic acid but, curiously, only forms two sodium salts, $Na_2H_2P_2O_7$ and $Na_4P_2O_7$. Salts such as $NaH_3P_2O_7$ and $Na_3HP_2O_7$ do not exist. When pyrophosphoric acid is heated,

**784. Metaphosphoric Acid $HPO_3$** is formed,

$$H_4P_2O_7 = H_2O + 2HPO_3.$$

Metaphosphoric acid is also made by heating orthophosphoric acid to a red heat, and is also obtained by the action of cold water on phosphorus pentoxide. It forms a deliquescent glassy mass. When boiled with water it forms orthophosphoric acid,

$$HPO_3 + H_2O = H_3PO_4.$$

Polymers of this acid, *e.g.*, the hexametaphosphates, are important in modern water-softening practice (*v.* § 243).

**785. Detection of the Phosphoric Acids and the Phosphates.**—Orthophosphates are detected by the *molybdate test* ; metaphosphates and pyrophosphates give it if their solutions are previously boiled with dilute acid to convert them into orthophosphoric acid.

The phosphate is dissolved in nitric acid and ammonium molybdate solution is added. On warming to about 60° C. a yellow precipitate of ammonium phosphomolybdate,

$$(NH_4)_3PO_4 . 12MoO_3$$

is produced. The test is given by other phosphorus compounds which are for the most part oxidised to phosphates by nitric acid. Arsenates give a similar precipitate but only on *boiling* the mixture.

Ortho-, pyro- and meta-phosphates are distinguished by their action upon silver nitrate and upon albumen. Orthophosphoric acid is the only one which gives a *yellow* precipitate with the former,

and metaphosphoric acid alone coagulates the latter. Their reactions may be summarised :—

| Acid. | Silver Nitrate. | Albumen. |
|---|---|---|
| Orthophosphoric acid . . | Yellow precipitate | No effect |
| Metaphosphoric acid . . | White „ | Coagulated |
| Pyrophosphoric acid . . | White „ | No effect |

The estimation of phosphates is carried out by precipitating them as magnesium ammonium phosphate, $MgNH_4PO_4 . 6H_2O$, by adding magnesium sulphate and ammonium chloride to the solution of phosphate made alkaline with ammonia,

$$NH_4^+ + Mg^{++} + PO_4^{---} = MgNH_4PO_4.$$

The magnesium ammonium phosphate is filtered off, dried, and heated to redness in a crucible, when magnesium pyrophosphate $Mg_2P_2O_7$ remains behind and is weighed.

**786. Phosphorus Sulphides.**—Numerous sulphides of phosphorus are known. They are prepared by cautiously heating sulphur and red phosphorus in a current of an inert gas, and may be purified by recrystallisation from carbon disulphide. The sulphides $P_2S_5$, $P_4S_7$ and $P_4S_3$ are definite chemical compounds.

*Phosphorus pentasulphide* $P_2S_5$ is a greyish-yellow crystalline substance, which reacts with water, forming orthophosphoric acid and hydrogen sulphide,

$$P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S.$$

It reacts with organic compounds in such a way as to replace a part of their oxygen by sulphur, and this is its only use.

*Phosphorus sesquisulphide* $P_4S_3$ forms a grey crystalline mass which is used in the manufacture of matches (§ 768).

## Phosphorus Halides

Phosphorus forms two compounds with each of the halogens, $PHa_3$, $PHa_5$. The existence of phosphorus pentaiodide is, however, rather doubtful.

*Phosphorus trifluoride* $PF_3$ can be made by heating lead fluoride and copper phosphide,

$$3PbF_2 + Cu_3P_2 = 3Pb + 3Cu + 2PF_3.$$

It is a colourless gas. With water if forms hydrofluophosphoric acid $HPF_4$ together with phosphorous acid,

$$2PF_3 + 3H_2O = H_3PO_3 + 2HF + HPF_4.$$

*Phosphorus pentafluoride* $PF_5$ can be prepared by the action of arsenic fluoride on phosphorus pentachloride. It is decomposed by water and is probably fairly stable.

*Phosphoryl fluoride* $POF_3$ is also a gas with reactions much like those of phosphoryl chloride.

*Thiophosphoryl fluoride* $PSF_3$ made by the action of phosphorus sulphide on lead fluoride is a gas remarkable in reacting with air and burning with a luminous but almost cold flame in which the hand may be held.

**787. Phosphorus Trichloride $PCl_3$.**—When chlorine acts upon an excess of phosphorus the trichloride is formed,

$$2P + 3Cl_2 = 2PCl_3.$$

The usual apparatus for its preparation is shown in Fig. 150. A layer of dry sand is placed in the bottom of the retort and on it is placed dry white phosphorus, say, 25 gms. Chlorine, which must be well-dried by sulphuric acid, is led over the phosphorus, which is gently warmed on a water bath. The distance of the chlorine tube from the melted phosphorus is so arranged that no phosphorus distils over, as occurs if it is too near, and also so that no solid pentachloride is formed, as occurs if it is too far away. At the end of the experiment a little further heating may be required.

The liquid so prepared contains some pentachloride, and this is best removed by redistilling it over white phosphorus.

Phosphorus trichloride is a heavy, colourless, fuming, mobile refractive liquid (D., 1·61), which boils at 74° C. and freezes at − 115° C. It is a typical chloride of a non-metal [1] and reacts with

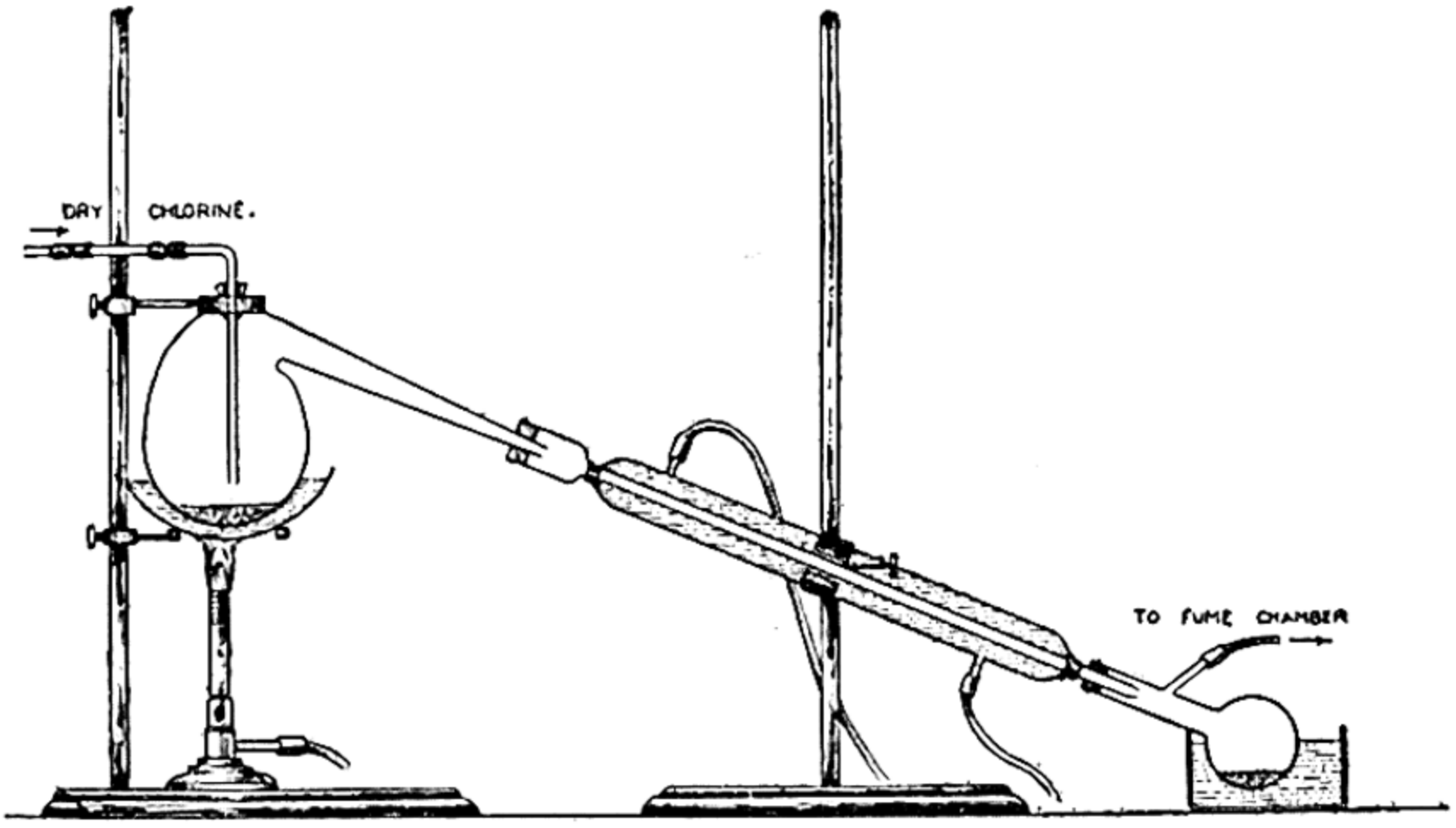



FIG. 150.—Preparation of phosphorus trichloride.

[1] Cf. chlorides of boron, silicon, sulphur, arsenic, and the chlorides of certain of the metals, as aluminium, tin, antimony.

water and with most substances containing the hydroxyl group, OH. In the reactions which ensue the hydroxyl groups and the chlorine atoms exchange places, a halide and phosphorous acid, $H_3PO_3$, being produced,

$$PCl_3 + 3HOH = P(OH)_3 + 3HCl$$

$$PCl_3 + 3C_2H_5 . OH = P(OH)_3 + 3C_2H_5 . Cl.$$

Ethyl alcohol. Ethyl chloride.

This property of replacing hydroxyl by chlorine makes it a valuable reagent in organic chemistry. Phosphorus trichloride reacts with chlorine, forming phosphorus pentachloride.

**788. Phosphorus Pentachloride.**—Phosphorus pentachloride is best prepared by passing a stream of chlorine gas over phosphorus trichloride until the latter is converted into a greenish crystalline mass. The apparatus figured may be used. A current of dry chlorine passes through the Woulffe's bottle and phosphorus trichloride is added drop by drop from a tap funnel,

$$PCl_3 + Cl_2 = PCl_5.$$

Phosphorus pentachloride is, when pure, a nearly colourless solid which sublimes at 100–160° C.; under pressure it melts at 148° C. It gives off copious and very irritating fumes when exposed to the air. When heated, phosphorus pentachloride vapour decomposes into chlorine and the trichloride,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2,$$

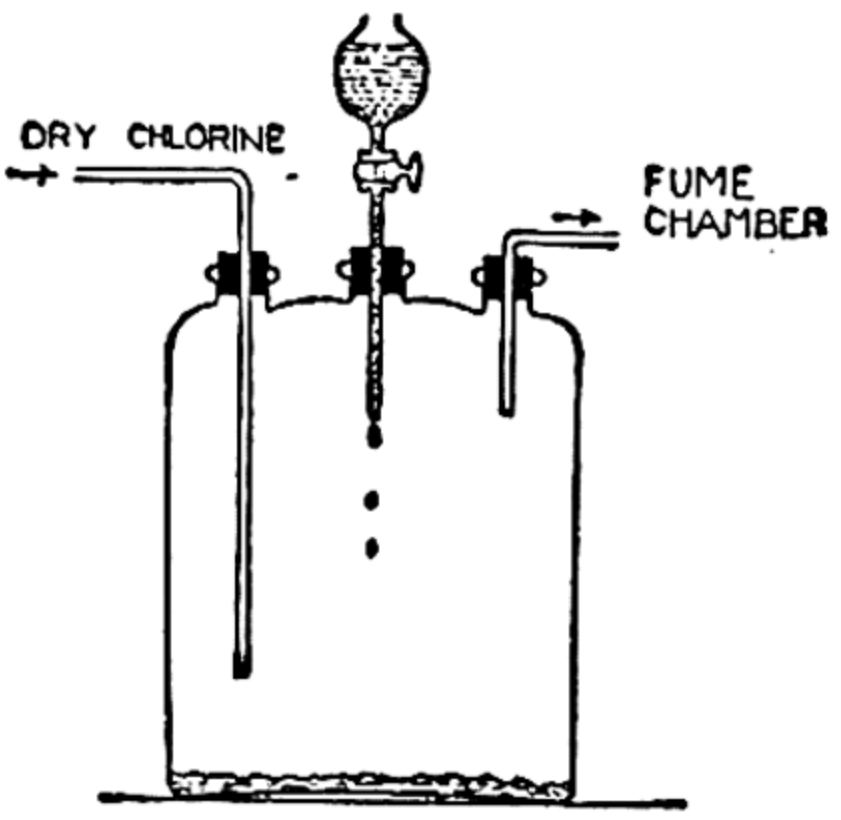
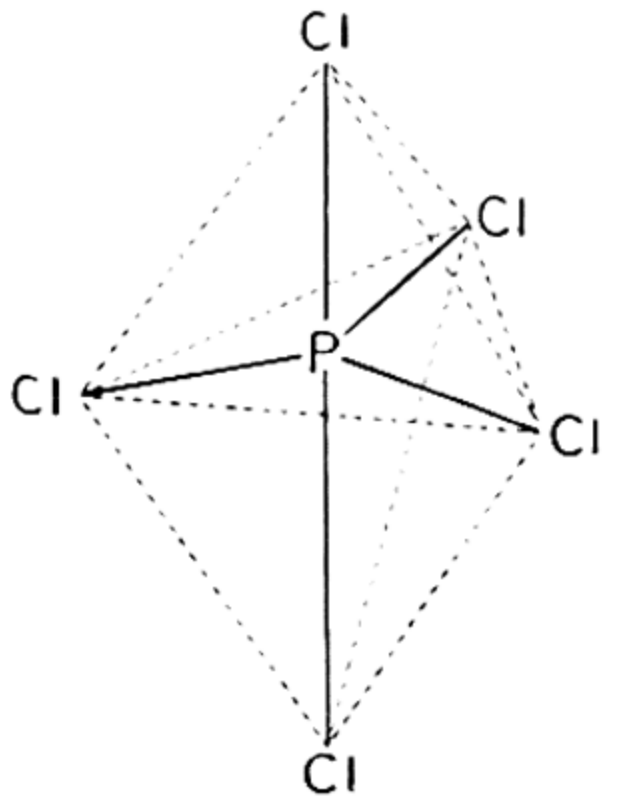



FIG. 151.—Preparation of phosphorus pentachloride.

and in consequence its vapour appears to have a density and molecular weight corresponding to a formula, $\frac{PCl_5}{2}$. If, however, the vapour density be measured at lower temperatures it tends towards the value corresponding to the formula $PCl_5$. (Cf. case of ammonium chloride, p. 524.)

The structure of phosphorus pentachloride is peculiar. In the state of vapour the five chloride atoms are attached by ordinary single covalent linkages, thus :—




while in the solid state it is an ionised salt-like compound $[PCl_4]^+ [PCl_6]^-$

When treated with water it reacts violently with a hissing sound and forms first phosphorus oxychloride and then orthophosphoric acid,

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$
$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

It reacts with hydroxyl compounds very vigorously and is the best reagent for preparing *acid chlorides*. Most anhydrous acids contain hydroxyl, *e.g.*, $SO_2(OH)_2$ sulphuric acid, $NO_2 . OH$ nitric acid, $CH_3CO . OH$ acetic acid, and these when treated with phosphorus pentachloride replace this hydroxyl group by chlorine,

$$SO_2 . (OH)_2 + 2PCl_5 = \underset{\text{Sulphuryl chloride.}}{SO_2Cl_2} + 2POCl_3 + 2HCl.$$

$$CH_3 . CO . OH + PCl_5 = \underset{\text{Acetyl chloride.}}{CH_3 . CO . Cl} + POCl_3 + HCl.$$

**789. Phosphorus Tribromide $PBr_3$** is best made by allowing bromine to act on yellow phosphorus covered by a layer of benzene. The solution is distilled. The benzene comes over at 80° C. and the tribromide distils over at 174° C.

It closely resembles the trichloride, but is denser (D., 2·93) and has a higher boiling point. Its reactions with water, hydroxyl compounds and with bromine are analogous to those of the trichloride.

**790. Phosphorus Pentabromide $PBr_3$** is made by the action of bromine on the tribromide. It is a yellow solid and resembles the pentachloride, although its reactions are less vigorous.

**791. Phosphorus Tri-iodide $PI_3$** is made by dissolving equivalent weights of iodine and of yellow phosphorus in carbon disulphide and mixing the solutions. It forms reddish crystals. Phosphorus di-iodide $P_2I_4$ is also known.

**792. Phosphorus Oxychloride, Phosphoryl Chloride $POCl_3$.**—This substance is best made by the action of potassium chlorate on phosphorus trichloride,

$$KClO_3 + 3PCl_3 = KCl + 3POCl_3.$$

It may also be made by the careful addition of water to phosphorus pentachloride,

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

It is a fuming liquid which boils at 107° C. With water it forms orthophosphoric and hydrochloric acids,

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

## ARSENIC As, 74·91

**793. Historical.**—The element arsenic was possibly prepared by the Greek alchemists, and it was certainly prepared as early as the thirteenth century by Albertus Magnus, or by someone who wrote under the name of that great man. The sulphides of arsenic, realgar and orpiment, were used by the Egyptians and later peoples as pigments for decorative frescoes, etc. The name 'arsenikon,' ἀρσενικὸν, given by the Greeks to orpiment, arsenious sulphide, means the 'male' or 'potent' substance, and is perhaps connected with the poisonous qualities of the arsenic trioxide easily obtained from it.

**794. Occurrence.**—Arsenic compounds are very widely distributed, and the ores of most metals contain small quantities. Most commercially prepared metals, therefore, contain a trace of arsenic. The chief source of arsenic is *mispickel* or arsenical pyrites, $FeS_2 . FeAs_2$. It occurs also as *realgar* $As_2S_2$, and *orpiment* $As_2S_3$. In the roasting of most ores of tin and copper, arsenic trioxide (*q.v.*) is produced and the supply much exceeds the demand. The disposal of this highly poisonous compound is a serious problem.

**795. Preparation of Arsenic.**—The element arsenic is prepared by heating mispickel in an earthenware retort, to the mouth of which is fitted a piece of thin sheet-iron rolled into a tube. The reaction $FeS_2 . FeAs_2 = 2FeS + 2As$ takes place and the arsenic condenses as a solid crystalline mass on the iron. Arsenic is also prepared industrially by heating sublimed arsenic trioxide with charcoal in closed retorts.

**796. Properties.**—The element arsenic exists in three forms. Grey or metallic arsenic is that commonly met with. When the element is sublimed in a current of hydrogen two unstable modifications condense: first, black crystals of β-arsenic, then a yellow powder of α-arsenic. Both varieties change back to the grey variety on standing. The yellow variety is soluble in carbon disulphide, therein resembling yellow phosphorus. Grey arsenic is a steel-grey solid of metallic appearance. It is odourless and tasteless, but its vapour has the odour of garlic. Arsenic is very brittle. It conducts electricity well. Arsenic volatilises from 100° C. upwards, but does not melt except under pressure; its melting point under pressure is 500° C.

In its physical properties it may, then, be regarded as definitely metallic in character.

Arsenic burns in air with a blue flame, producing arsenic trioxide

$$4As + 3O_2 = 2As_2O_3.$$

It reacts with chlorine—igniting if powdered—forming arsenic trichloride.

$$2As + 3Cl_2 = 2AsCl_3.$$

It also reacts with the other halogens and with sulphur.

Acids which are not also oxidising agents do not affect it, and therein it resembles a non-metal. Fairly concentrated nitric acid oxidises it to arsenious oxide and finally to arsenic acid. *Aqua regia* also oxidises the element.

**797. Atomic Weight.**—That the atomic weight of arsenic is about 75 follows from the molecular weights of its volatile compounds, the gram-molecular weight of which never contains less than 75 gms. of arsenic (§ 62). This value follows also from its position in the periodic table and from Dulong and Petit's law. Accurate determinations of its atomic weight have been made by several methods, such as the conversion of silver arsenate $Ag_3AsO_4$ into silver bromide AgBr, and silver chloride AgCl. It does not appear to have any isotopes. The best value for its atomic weight appears to be 74·91.

**798. Arsenic Hydride, Arsine, $AsH_3$.**—Arsenic forms one hydride, $AsH_3$, which is of considerable interest.

Arsine is prepared by the reduction of arsenic compounds by nascent hydrogen, as in the Marsh test described below,

$$As_2O_3 + 12H = 2AsH_3 + 3H_2O.$$

A gas mixed with very little hydrogen is obtained by the action of an acid upon magnesium or calcium arsenides.

$$Mg_3As_2 + 6HCl = 3MgCl_2 + 2AsH_3.$$

It may be obtained quite pure by freezing out moisture, then liquefying the gas by further cooling to —100° C.

Arsenic hydride is evolved in small quantities by certain moulds in contact with arsenic compounds. A scare was caused during the last century concerning the danger of green wallpapers coloured with arsenical pigments, such as Schweinfurth green. It was alleged that these when damp and mouldy gave off arsenic hydride and caused arsenic poisoning in those who inhabited rooms so papered.

Arsenic hydride is a colourless gas, with an unpleasant smell. It is exceedingly poisonous even when much diluted with air.

Arsenic hydride is very unstable. When heated to about 230° C. it decomposes into the element arsenic and hydrogen,

$$2AsH_3 = 2As + 3H_2.$$

It is a powerful reducing agent. With silver nitrate it gives a yellow

coloration, due to the compound $Ag_3As \cdot 3AgNO_3$, which gradually blackens owing to decomposition to silver.

Arsenic hydride is utilised in the Marsh test for the detection of

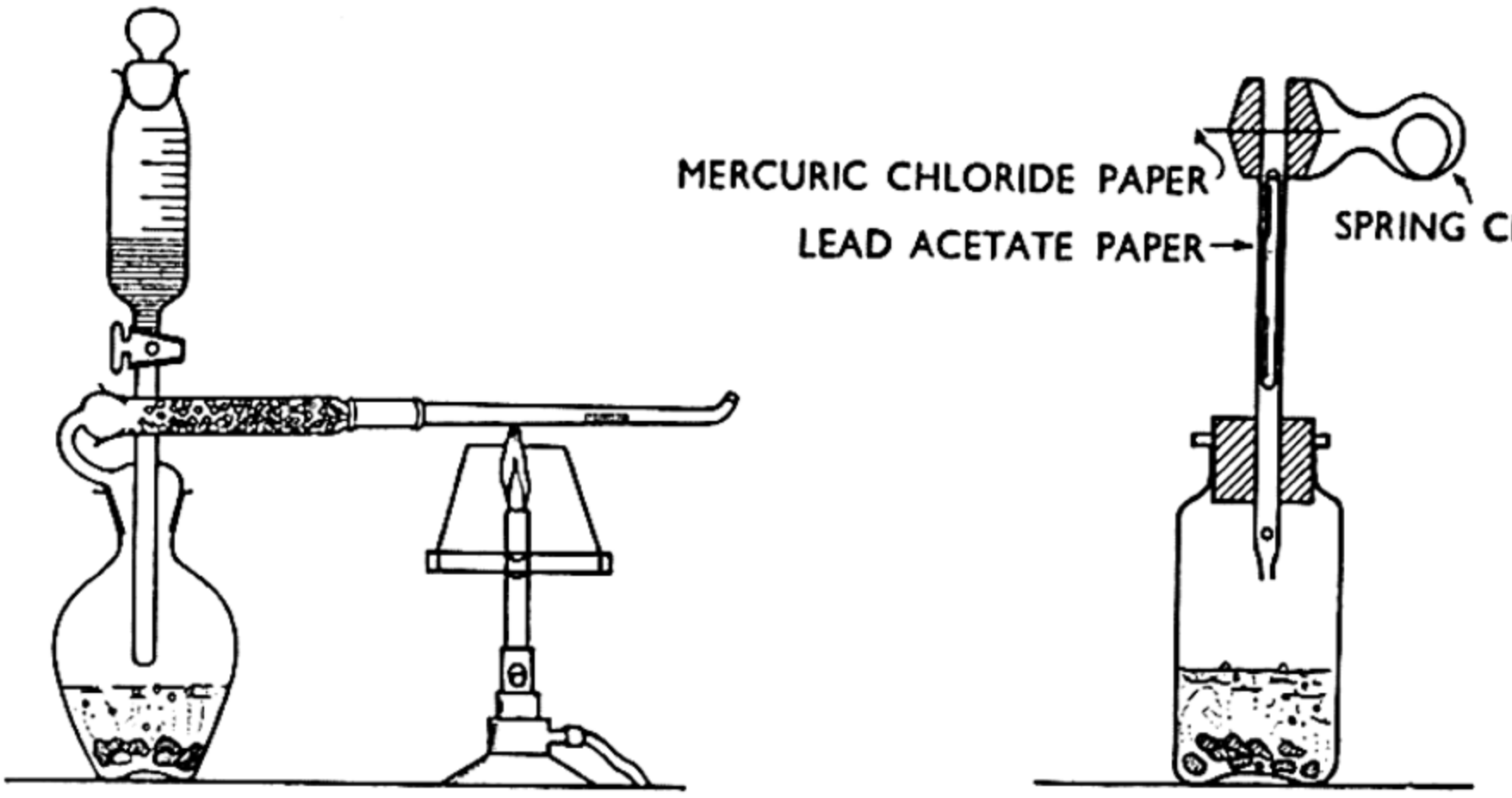



FIG. 152.—Marsh test for arsenic.

arsenic. In this test hydrogen is generated in a small flask (either from arsenic-free zinc and arsenic-free acid or by electrolysis), and then passed along a glass tube heated at one point by a minute flame. The solution suspected of containing arsenic is run into the flask and the arsenic, if present, forms arsine. The arsine is decomposed at the hot point in the tube and the arsenic so produced deposits just beyond this point as a dark shining 'mirror.' The amount of arsenic present may be obtained by comparing the mirror with standard mirrors prepared from known weights of arsenic.

Antimony compounds produce a similar mirror, but these mirrors are insoluble in sodium hypochlorite solution, which rapidly dissolves metallic arsenic. The test is exceedingly delicate and it is difficult to procure materials for the generation of hydrogen so pure as to give no arsine in this test.

The form of the Marsh test which is now most in use for testing food and drugs for traces of arsenic is that prescribed in the British Pharmacopœia. A bottle holding 120 c.c. contains 10 gms. of arsenic-free zinc (AsT quality). A rubber bung is fitted with an upright tube 20 cm. long with a side hole to prevent liquid being carried up it. The tube contains a lead acetate paper rolled into a cylinder 10 cm. long. Two perforated rubber bungs at the top are held together by a spring clip and enclose a sheet of paper which has been moistened with saturated mercuric chloride solution and dried. The solution suspected of containing arsenic is mixed with about one-fifth of its weight of arsenic-free (AsT) hydrochloric acid and a

little stannous chloride, which serves to reduce pentavalent arsenic compounds.

It is poured on the zinc: the hydrogen with any arsine formed passes through the circle of mercuric chloride paper, and if arsenic is present a yellow stain is caused. This is compared with the stains caused by various minute known quantities of arsenic, and the proportion of arsenic in the solution is thus ascertained.

The composition of the yellow substance is still in doubt.

**799. Arsenic Trioxide, White Arsenic, Arsenious Anhydride $As_2O_3$.**—Arsenic trioxide is commonly known as 'arsenic,' and is the most important compound of that element. It was known to the Greek alchemists (A.D. 100 onward), but does not seem to be mentioned by any earlier ancient authors.

*Manufacture.*—Arsenious oxide is prepared by roasting mispickel, $FeS_2 . FeAs_2$,

$$FeS_2 . FeAs_2 + 5O_2 = Fe_2O_3 + 2SO_2 + As_2O_3.$$

The ore is frequently roasted in a revolving calciner (Fig. 153) down which the ore travels, while the furnace gases and arsenic trioxide vapour pass upwards and into a series of brick chambers, where the arsenic condenses as a grey powder containing carbon, etc. This may be resublimed in a cast-iron pan surmounted by a bell, on which the arsenic condenses as a transparent glass—vitreous arsenic.

Alternatively it is sublimed from a reverberatory furnace (Fig. 123) into brick chambers, much as in the preparation of the crude material.

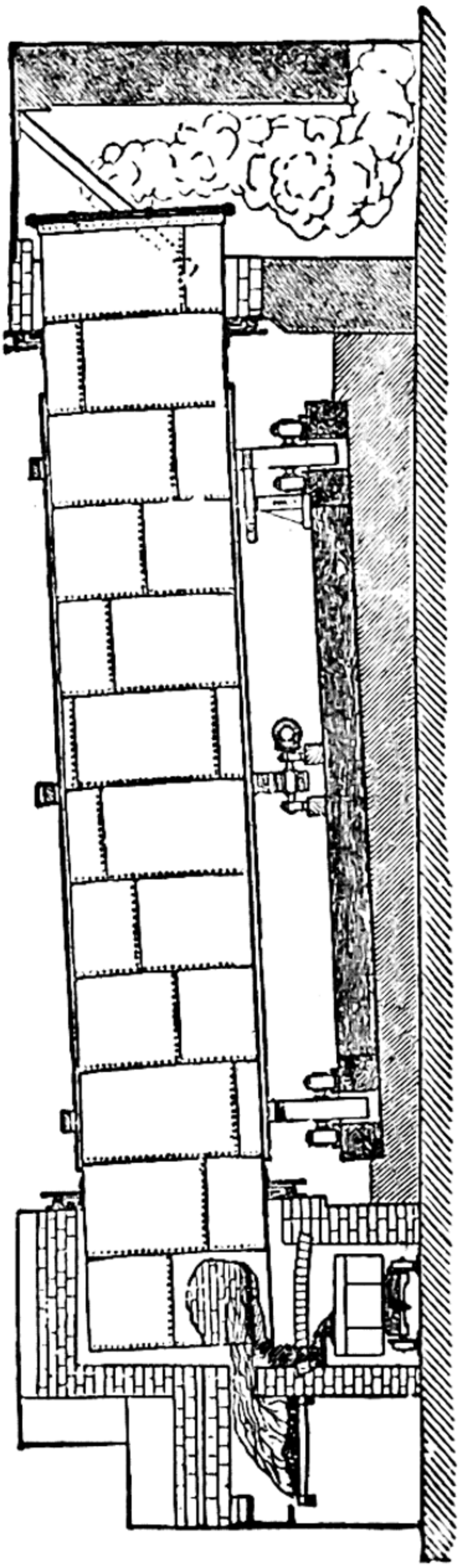


Fig. 153.—Revolving calciner for roasting of arsenic ores.

*Properties.*—Arsenic trioxide exists in three forms :—

(1) Vitreous arsenic trioxide (amorphous arsenic trioxide).

(2) Octahedral or common arsenic trioxide.

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(3) Orthorhombic prisms.

Vitreous arsenic trioxide is a transparent glassy solid. In presence of moisture it soon becomes opaque and is transformed into octahedral arsenic trioxide. The vitreous form is more soluble in water (1 : 108) than the octahedral form (1 : 355), as is to be expected, seeing that it is the less stable form.

If the vitreous form (3 parts) be dissolved in hot diluted hydrochloric acid (12 acid, 4 water) the octahedral form crystallises out, each crystal giving a flash of light as it is formed. The exact cause of this phenomenon is not clear, but the light may result from the chemical energy liberated when the amorphous form changes to the more stable octahedral modification.

Octahedral arsenic is a crystalline powder. The crystals are highly refractive and brilliant.

It is without odour and tasteless—an assertion which the student is not recommended to test. Arsenic trioxide is highly poisonous, from 0·3 to 0·4 gm. being a fatal dose. It is often used criminally, since it is one of the few powerful poisons easily obtainable and free from taste or smell. Fortunately, its detection is very easy, even a long time after the death of the victim. It is remarkable that it is eaten habitually by certain people without harm resulting, as much as half a gram being taken at once. The cause of this apparent immunity is probably not the habituation of the body to the poison, but is merely the effect of the insoluble character of the coarsely crystalline arsenic eaten; very little being actually assimilated. The inhabitants of Styria (S. Austria) formerly used it in this way to improve their 'wind' and endurance. It appears to have little, if any, ill-effect if an overdose is not taken. The best antidote to arsenic poisoning is ferric hydroxide in any form, 'dialysed iron,' etc.; it must be taken quickly if it is to be effective. The insoluble and comparatively harmless ferric arsenite is produced,

Arsenic trioxide volatilises without fusion at about 109° C., but if the pressure is raised the oxide fuses. This behaviour is due to the fact that the melting point of arsenic trioxide is higher than its boiling point at atmospheric pressure, but lower than its boiling point at, say, 2 atm.

Arsenious oxide is soluble in water. The different forms have different solubilities. Octahedral arsenic trioxide is the least soluble of these and at 15° C. 100 gms. of water dissolve 1·66 gms.; at 100° C. 100 gms. of water dissolve 6·00 gms. of the solid.

*Chemical Properties.*—Arsenic trioxide is an acidic oxide with only slight basic properties. It dissolves in water to form a weakly acid

solution, probably containing arsenious acid,

$$As_2O_3 + 3H_2O \rightleftharpoons 2H_3AsO_3.$$

With alkalis it forms various *arsenites*, usually of complex formulæ,

$$As_2O_3 + 6KOH = 2K_3AsO_3 + 3H_2O$$
$$2As_2O_3 + 2KOH = K_2As_4O_7 + H_2O$$
$$2As_2O_3 + 6KOH = K_6As_4O_9 + 3H_2O.$$

Arsenic trioxide is readily oxidised to arsenic pentoxide or to arsenic acid. Nitric acid does this, being itself reduced to various oxides of nitrogen (§ 801). The halogens also oxidise arsenic trioxide. Iodine is used to estimate arsenious acid volumetrically ;

$$As_2O_3 + 4I + 2H_2O \rightleftharpoons As_2O_5 + 4HI$$
$$(As_2O_5 + 3H_2O = 2H_3AsO_4).$$

The reaction goes to completion in presence of sodium bicarbonate, which removes the hydrogen iodide, but unlike the caustic alkalis does not react with iodine.

Arsenious oxide behaves like a basic oxide in its reaction with concentrated hydrochloric acid, arsenic trichloride being formed,

$$As_2O_3 + 6HCl \rightleftharpoons 2AsCl_3 + 3H_2O.$$

It reacts with hydrogen sulphide,

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

The arsenic sulphide may deposit as a yellow solid or remain in colloidal solution. This solution is one of the easiest sols to prepare.

Arsenic trioxide finds numerous uses in industry, in glass-making, pyrotechny and as a poison for plants and animals. Fly papers, rat poisons, and arsenical soap for preserving skins contain it.

*Fowler's solution* is a weak solution of sodium arsenite, used mainly in veterinary medicine as a tonic. Arsenious oxide is used in making arsenic acid and the arsenites mentioned below.

Arsenic trioxide has caused poisoning by its accidental presence in foodstuffs. In the year 1900 about 6,000 people suffered illness and some 70 died from arsenic poisoning, the origin of which was beer. The arsenic is said to have been introduced into the beer with glucose manufactured from sulphuric acid containing arsenic, originally derived from arsenical pyrites.

Recently a number of children in the Potteries district were made ill as a result of eating sweets dusted with arsenic trioxide, which had been mistaken for French chalk.

**800. The Arsenites.**—Some of the salts of arsenious acid are of special interest. The arsenites may be regarded as derived from the acids $As_2O_3 . H_2O$ or $HAsO_2$ and the acid $As_2O_3 . 3H_2O$ or $H_3AsO_3$.

*Sodium arsenite*, as made by dissolving arsenious oxide in caustic soda, is an acid salt. The neutral salt $NaAsO_2$ can be made by boiling this with sodium carbonate solution.

Sodium arsenite is used as a weed-killer. It is, of course, highly poisonous. When treated with an acid, arsenious oxide is produced,

$$2NaAsO_2 + 2HCl = 2NaCl + H_2O + As_2O_3.$$

*Copper arsenite* $CuHAsO_3$ is made by dissolving arsenic trioxide in potassium carbonate solution and adding copper sulphate solution to the potassium arsenite so formed.

It is a fine green pigment, known as *Scheele's green*. Its very poisonous character has led to its disuse.

*Copper aceto-arsenite* $Cu(C_2H_3O_2)_2 . 3Cu(AsO_2)_2$ is a fine green pigment, and is made by mixing sodium arsenite and copper acetate in the correct proportions. Its use in wallpaper (*v. supra*) may cause the production of arsine or diethylarsine $HAs(C_2H_5)_2$.

**801. Arsenic Oxide, Arsenic pentoxide $As_2O_5$.**—This oxide is made by oxidising arsenious oxide with concentrated nitric acid, nitrogen peroxide being evolved,

$$As_2O_3 + 4HNO_3 = As_2O_5 + 2H_2O + 4NO_2,$$

or by passing chlorine through a suspension of the oxide in water.

$$As_2O_3 + 2Cl_2 + 2H_2O = As_2O_5 + 4HCl.$$

The solutions are evaporated to dryness.

Arsenic pentoxide is a white solid. It has an acid taste and is poisonous, though to a less extent than the trioxide.

Arsenic pentoxide dissolves readily in water, and the solution contains arsenic acid,

$$As_2O_5 + 3H_2O \rightleftharpoons 2H_3AsO_4.$$

*The Arsenates.* Crude sodium arsenate is made by heating solid arsenic with sodium nitrate.

In the laboratory it may be made by mixing a solution of arsenic acid with excess of sodium carbonate and allowing the sodium arsenate $Na_2HAsO_4 . 12H_2O$ to crystallise out. It is a stable salt, much resembling sodium phosphate. It finds a use in calico-printing.

*Lead arsenate* is used for spraying fruit trees. It does not harm the trees but kills the caterpillars which eat the sprayed leaves. Accidents have resulted from small quantities lodging in the depression at the top of an apple. Needless to say, the spraying should be done before the fruit has set.

**802. Arsenic Sulphides.**—These are three :—

| | |
|---|---|
| Arsenic disulphide, realgar . . . | $As_2S_2$ |
| Arsenic trisulphide, orpiment . . | $As_2S_3$ |
| Arsenic pentasulphide . . . | $As_2S_5$ |

**803. Arsenic Disulphide, Realgar $As_2S_2$.**—This substance is found native as *ruby sulphur*, but is usually made by fusing together arsenic and orpiment, or sulphur,

$$2As_2S_3 + 2As = 3As_2S_2$$
$$2S + 2As = As_2S_2.$$

Realgar is a hard brittle orange-red substance. It readily burns in air,

$$2As_2S_2 + 7O_2 = 2As_2O_3 + 4SO_2.$$

It is very unreactive, and is not easily attacked by acids, etc., but is readily oxidised by nitric acid.

It is used for making ' blue fire ' and ' white fire ' in pyrotechny, and it also finds a use as a pigment.

**804. Arsenic Trisulphide, Orpiment.**—The name orpiment is a corruption of the Latin ' auripigmentum,' gold paint.

Arsenic trisulphide is found native but is usually made by subliming a mixture of arsenious oxide and sulphur,

$$2As_2O_3 + 9S = 2As_2S_3 + 3SO_2.$$

In the laboratory it is readily made by the action of hydrogen sulphide on a solution of arsenious oxide in hydrochloric acid,

$$2AsCl_3 + 3H_2S \rightleftharpoons As_2S_3 + 6HCl.$$

Arsenic trisulphide is a fine yellow solid. It sublimes when heated, and if air is present it forms arsenic trioxide.

$$2As_2S_3 + 9O_2 = 2As_2O_3 + 6SO_2.$$

Arsenic trisulphide is insoluble in water. It is an ' acidic sulphide ' and is readily soluble in solutions of alkaline sulphides. Thus it dissolves in sodium sulphide solution, forming sodium thioarsenite,

$$Na_2S + As_2S_3 = 2NaAsS_2.$$

Yellow ammonium sulphide, which contains sulphur in solution, *oxidises* it and forms ammonium thioarsenate,

$$3(NH_4)_2S + 2S + As_2S_3 = 2(NH_4)_3AsS_4.$$

These reactions are of some interest as they are used in qualitative analysis.

**805. Arsenic Pentasulphide $As_2S_5$** is obtained by passing a rapid stream of hydrogen sulphide through a solution of arsenic acid mixed with twice its volume of concentrated hydrochloric acid,

$$2H_3AsO_4 \rightleftharpoons As_2O_5 + 3H_2O$$
$$As_2O_5 + 5H_2S = As_2S_5 + 5H_2O.$$

It is a bright yellow solid, decomposed on heating into arsenic trisulphide and sulphur.

**806. Other Salts of Arsenic.**—Arsenic does not form oxysalts, such as nitrates, sulphates, etc., and therein shows its chemical character as a non-metal.

**807. Arsenic Chloride.**—Arsenic trichloride is prepared by the action of chlorine on arsenic, or better, by heating sulphur chloride with arsenic trioxide in a flask fitted with reflux condenser, a current of chlorine being passed. The arsenic chloride is distilled over.

$$4As_2O_3 + 3S_2Cl_2 + 9Cl_2 = 8AsCl_3 + 6SO_2.$$

The action of concentrated hydrochloric acid upon arsenious oxide gives a solution of the compound.

It is a colourless liquid. It has strong corrosive properties and has been used as a caustic. Arsenic trichloride boils at 130° C.

It is hydrolysed by water, the reaction being reversible,

$$2AsCl_3 + 6H_2O \rightleftharpoons 2H_3AsO_3 + 6HCl.$$

Arsenic trichloride is intermediate in type between the typical non-metallic chloride, such as phosphorus trichloride, and the typical metallic chlorides, such as those of zinc or copper. Its solutions behave like those of metallic salts in some respects. They do not, however, appear to contain the ion $As^{+++}$.

It should be noted that there is no compound $AsCl_5$. The only known halogen compound of pentavalent arsenic is the pentafluoride $AsF_5$.

**808. Detection of Arsenic.**—The Marsh test has already been described (§ 798). The Reinsch test is for some purposes preferred to the Marsh test. The solution of the substance suspected to contain arsenic is warmed with concentrated arsenic-free hydrochloric acid and a piece of pure bright copper foil. The copper becomes covered with a dark layer of copper arsenide and is then dried, placed in a glass tube, and gently heated in a slow current of hydrogen. The arsenic, if present, sublimes from the copper and forms a mirror on the tube walls.

## ANTIMONY Sb, 121·76

**809. Historical.**—The element antimony was known to the ancients, though it was confused with lead. Antimony sulphide,

the Greek στίμμι, and the Latin *stibium*, has been used in the East as an eyebrow-black since the remotest times. Pliny speaks of the 'lead' made from stibium, and clearly refers to metallic antimony. The name antimony is a curious one. The suggestion that it was called *anti-moine* because a number of monks were accidentally poisoned with it, seems to have no foundation. Probably the name was derived from some such word as ἀντεμονίον, connected with the Greek ἄνθος, a flower, the word *flower* being used for a fine powder, *e.g.*, flowers of sulphur. To the alchemist Basil Valentine is attributed a book entitled "The Triumphal Chariot of Antimony," in which he extolled its remarkable properties. This is doubtless a forgery dating from the beginning of the seventeenth century. It is, however, full of interest for the early history of this element.

**810. Occurrence.**—Metallic antimony is rarely found native. Its most important ore is *stibnite*, antimony sulphide; but it is found in numerous other forms, as oxide $Sb_2O_3$, etc.

**811. Manufacture of Antimony.**—Stibnite is treated in two ways. If the ore is of good quality it is usually smelted by heating it with scrap iron. Iron sulphide and antimony result,

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS.$$

The antimony settles to the bottom. It is purified by re-melting it with some more sulphide and a little salt.

A poor ore is often treated by roasting it and oxidising it to trioxide, which is condensed as a solid in much the same way as is arsenic trioxide. The oxide is then reduced with carbon, either in a reverberatory furnace or in crucibles,

$$2Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2$$
$$2Sb_2O_3 + 3C = 4Sb + 3CO_2.$$

*Properties.* Antimony is a greyish metal of considerable lustre. When pure it crystallises very well and ingots of antimony are known to be pure if they show a beautiful 'star' or 'fern-leaf' on the surface. Antimony is a very brittle metal, of density 6·8, which melts at 630° C. It is valuable for castings, as it expands on solidifying and takes a particularly good impress of the mould. Antimony-lead alloys—type-metal—also expand in this way, and their value for casting type depends on the property. For a metal antimony is a poor conductor of heat and electricity.

**812. Allotropy.**—Antimony, like arsenic, exists in three allotropic forms :—

(1) Crystalline metallic antimony, which has already been described.

(2) Yellow modification (only stable at low temperatures).
(3) Explosive or amorphous antimony.

The last is obtained by the slow electrolysis of a solution of antimony trichloride in hydrochloric acid. It has a steel-like lustre. When heated or even scratched with a nail, it changes to the crystalline form, producing much heat. This modification is never free from antimony trichloride and hydrogen chloride.

**813. Chemical Properties.**—Antimony burns at a red heat, giving off white fumes of the trioxide.

$$4Sb + 3O_2 = 2Sb_2O_3.$$

It combines readily with the halogens, thus powdered antimony ignites in chlorine. It also combines readily with sulphur.

Antimony is not affected by dilute acids other than nitric acid. Concentrated hydrochloric and sulphuric acid produce their respective salts,

$$2Sb + 6HCl = 2SbCl_3 + 3H_2.$$

Antimony is between bismuth and hydrogen in the electromotive scale. Thus it is displaced from solutions of its salts by most metals. Antimony finds uses in the making of certain alloys.

Alloyed with lead, it hardens it and also makes the melted lead more fluid. Lead for the manufacture of shot accordingly contains antimony. Type metal, Britannia metal and some anti-friction metals contain antimony. With copper, antimony forms a remarkable alloy, 'Regulus of Venus,' which is violet in colour. It is apparently a compound, $SbCu_2$

**814. Atomic Weight.**—Antimony must, from the law of Dulong and Petit and from the densities of its volatile compounds and its position in the Periodic table, have an atomic weight of about 120. From this value and the equivalent (*c.* 40) it is evident that antimony is tervalent in certain of its halides, and the formula of the ordinary chloride is evidently $SbCl_3$. Its atomic weight has been determined by converting the metal into the chloride, and by precipitating silver chloride from antimony chloride, etc. Results obtained by different workers varied rather considerably and a value of 120·2 was for a long time accepted. Recently the study of mass spectra revealed the existence of two isotopes of atomic weight, 121 and 123. The value for the atomic weight had therefore to lie between these figures, and determinations by three independent sets of workers agreed in giving values between 121·74 and 121·773. The value 121·76 is now adopted.

**815. Antimony Hydride, Stibine $SbH_3$.**—Antimony hydride is made by the same methods as arsenic hydride.

Stibine is a colourless gas with an unpleasant smell. It is poisonous. It decomposes even at room temperature and the pure gas may explode if heated,

$$2SbH_3 = 2Sb + 3H_2.$$

It has strong reducing properties. It differs from arsine in that it reacts with silver nitrate, forming silver antimonide $Ag_3Sb$, and not metallic silver as does arsine. These differences have been used to separate arsenic and antimony in qualitative analysis.

**816. Oxides of Antimony.**—These are three in number :—

| | |
|---|---|
| Antimonious oxide, antimony trioxide . | $Sb_4O_6$ |
| Antimony tetroxide . . . . | $Sb_2O_4$ |
| Antimony pentoxide . . . . | $Sb_2O_5$ |

**817. Antimony trioxide $Sb_2O_3$** is made by the action of water on antimony trichloride. A solution of the latter in hydrochloric acid is largely diluted, when the oxychloride is formed,

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl,$$

as a white precipitate. If this precipitate is filtered off and washed with water on the filter until the filtrate is no longer acid, the trioxide remains,

$$2SbOCl + H_2O \rightleftharpoons Sb_2O_3 + 2HCl.$$

Antimony trioxide is a white solid. It fuses when heated and sublimes below a red heat. If heated in air it reacts with oxygen, forming the tetroxide,

$$2Sb_2O_3 + O_2 = 2Sb_2O_4.$$

Antimony trioxide is slightly soluble in water and with alkalis gives *antimonites*, such as $NaSbO_2$, $Na_2Sb_4O_7$, etc. These salts are easily oxidised to *antimonates*.

Like arsenious oxide, it is attacked by hydrochloric acid, though more readily ; other acids have little or no effect.

**818. Antimony Tetroxide $Sb_2O_4$** is made by heating antimony or antimony trioxide in air,

$$2Sb + 2O_2 = Sb_2O_4.$$

Antimony tetroxide is a white solid, which is not volatile even at a red heat. It is acidic in character and forms salts when fused with potash. It is a mixed anhydride quite analogous to $N_2O_4$ and $P_2O_4$.

**819. Antimony Pentoxide $Sb_2O_5$.**—Antimony pentoxide may be made by the action of a large volume of water on antimony pentachloride,

$$2SbCl_5 + 5H_2O = Sb_2O_5 + 10HCl.$$

It forms a yellow powder which at a red heat loses oxygen and forms the tetroxide. It is very slightly soluble in water, forming an acid solution.

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**820. The Antimonates.**—Numerous antimonates exist. Potassium pyro-antimonate (sometimes called metantimonate) $K_4Sb_2O_7$ is made by fusing potassium nitrate and adding powdered antimony. When boiled with water, potassium dihydrogen pyro-antimonate is produced. A solution of this salt gives with sodium salts a precipitate of sodium dihydrogen pyro-antimonate, almost the only insoluble salt of that metal.

**821. Antimony Sulphides.**—Two sulphides of antimony exist :—

| | |
|---|---|
| Antimony trisulphide . . . . | $Sb_2S_3$ |
| Antimony pentasulphide . . . | $Sb_2S_5$ |

*Antimony trisulphide* occurs in two forms, one orange and the other black. The black form is the commonest ore of antimony—stibnite.

Antimony sulphide may be prepared in its black form by heating a mixture of powdered antimony and sulphur. The orange form is prepared by the action of hydrogen sulphide on a solution of antimony trichloride,

$$2SbCl_3 + 3H_2S \rightleftharpoons Sb_2S_3 + 6HCl.$$

Since the reaction is reversible, the solution of the trichloride used should not contain too much acid. Failure to precipitate antimony in qualitative analysis is usually due to this cause.

The orange form, when heated, is converted into the black.

Antimony trisulphide burns when heated in air, forming either the trioxide or tetroxide,

$$2Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2$$
$$Sb_2S_3 + 5O_2 = Sb_2O_4 + 3SO_2$$

Its ready combustibility makes it valuable in the preparation of match-heads, fireworks, percussion caps, etc.

Antimony sulphide dissolves in concentrated hydrochloric acid, giving the chloride and hydrogen sulphide. It is soluble in solutions of alkaline sulphides in precisely the same way as is arsenic sulphide (§ 804), *thioantimonites* being formed. Potassium thio-antimonite is the chief constituent of *Kermes mineral*, used medically in the eighteenth century. Various orange and red pigments are made from antimony sulphide by oxidising it by fusion in air, etc. The mixtures of oxide and sulphide so produced are of fine yellow, orange or vermilion tints.

Lead antimonate is also used as a yellow pigment.

**822. Antimony Pentasulphide $Sb_2S_5$** is made by boiling the trisulphide with caustic potash and sulphur and then acidifying the solution with sulphuric acid. Potassium sulphide is formed,

$$6KOH + 4S = K_2S_2O_3 + 2K_2S + 3H_2O.$$

This, with the trisulphide, forms the thioantimonite,

$$3K_2S + Sb_2S_3 = 2K_3SbS_3.$$

The sulphur present oxidises this to thioantimonate,

$$K_3SbS_3 + S = K_3SbS_4,$$

which when acidified gives antimony pentasulphide,

$$2K_3SbS_4 + 6HCl = 6KCl + Sb_2S_5 + 3H_2S.$$

It is a golden yellow substance. It combines with alkaline sulphides, forming thioantimonates, of which Schlippe's salt, $Na_3SbS_4 . 9H_2O$, is the best known. It has been used in the vulcanisation of rubber.

Recent work indicates that 'antimony pentasulphide' is not a true compound but rather a mixture of a tetrasulphide, $Sb_2S_4$, and sulphur.

## 823. Tartar Emetic.

### Potassium Antimonyl Tartrate $2[K(SbO) . C_4H_4O_6] . H_2O$.

This is a double salt of potassium tartrate and *antimonyl tartrate* or antimony oxytartrate. It is prepared by the action of acid potassium tartrate, 'cream of tartar,' on antimonious oxide. The equations are more easily followed if tartaric acid $C_4H_6O_6$ is called $H_2T$, where $T$ is $C_4H_4O_6$.

$$2KHT + Sb_2O_3 = 2K(SbO)T + H_2O.$$

Tartar emetic forms distinct and well-formed octahedral crystals, readily soluble in water. It has an unpleasant metallic taste. In small doses, 0·05–0·1 gm., tartar emetic causes vomiting and is sometimes used in medicine for this purpose ; larger doses are poisonous. It has recently found uses in treating tropical diseases, *e.g.*, kala-azar and bilharziasis. Large quantities are used as a mordant in dyeing.

**824. Antimony Chlorides.**—Two chlorides of antimony exist, the trichloride $SbCl_3$, and the pentachloride $SbCl_5$.

The trichloride is best prepared by the action of concentrated hydrochloric acid on antimony sulphide. A few drops of nitric acid accelerate the reaction.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

The solution obtained is evaporated until it crystallises. It is then distilled, and after a drop of the distillate has solidified on cooling, the pure antimony chloride is collected.

It can also be prepared by the action of chlorine on antimony or antimonious oxide.

Antimony trichloride is a white solid. It is buttery in consistency if not quite pure, and is given the trivial name of "Butter of antimony." It melts at 73° C. when pure and boils at 223·5° C. It is highly deliquescent.

Water decomposes it according to the reversible reaction,

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl,$$

the white insoluble antimony oxychloride being produced. It

resembles in most of its reactions a metallic chloride rather than that of a non-metal, though in its ready hydrolysis it shows a resemblance to the latter.

It finds uses in the making of antimonious oxide, used to prepare tartar emetic.

*Antimony pentachloride* $SbCl_5$ is prepared by passing chlorine into melted antimony trichloride. It finds some uses in the manufacture of organic chemicals.

**825. Antimony Oxychloride. Basic Antimony Chloride SbOCl.**—This substance is also known as *powder of Algaroth*, being so named from Vittorio Algarotto, a seventeenth-century exponent of its medicinal virtues. It is made by adding water to the trichloride till the solution is just turbid and then diluting the whole to about seven times its volume,

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl.$$

If too much water is used the trioxide (*q.v.*) is formed.

It is a white powder. It dissolves in hydrochloric acid and forms the trichloride according to the equation given above.

**826. Detection of Antimony.**—Antimony salts are easily detected by their precipitation of the orange sulphide when hydrogen sulphide is passed through their solutions, which should not have an acidity greater than 2–3 N. They are distinguished from arsenic compounds by the insolubility of this sulphide in saturated ammonium carbonate solution.

The Marsh test (*q.v.*) also serves to detect antimony.

## BISMUTH Bi, 209·0

**827. Historical.**—The element bismuth was known in the fourteenth century, but it was not satisfactorily studied until the eighteenth century.

**828. Occurence and Manufacture.**—Bismuth is not infrequently found native in small quantities in numerous minerals. The chief ores are bismuthyl carbonate and bismuth sulphide. The metal is obtained from them by smelting in small reverberatory furnaces with scrap-iron, lime, soda ash, and coke.

$$Bi_2S_3 + 3Fe \rightarrow 2Bi + 3FeS$$
$$(BiO)_2CO_3 + 4C \rightarrow 2Bi + 5CO$$

Alternatively the ores are roasted to the oxide, which is taken up in hydrochloric acid. On diluting the solution bismuth oxychloride is precipitated. This is filtered and washed with hot water to remove lead chloride, and then smelted with limestone and charcoal to give metallic bismuth.

$$4BiOCl + 2CaCO_3 + 3C \rightarrow 4Bi + 2CaCl_2 + 5CO_2$$

The bismuth produced by this method is much purer than that produced by direct smelting, and the process can in fact be used as a method of refining the metal. Bismuth is also extracted from the anode slimes in the electrolytic refining of lead.

**829. Properties of Bismuth.**—Bismuth is a grey-white metal with a pink tinge. It readily crystallises. The method used for preparing crystals of monoclinic sulphur (§ 887) will afford good crystals of bismuth. Bismuth is one of the most fusible of metals, melting at 264° and boiling about 1,420° C.

Bismuth is brittle and of poor tenacity. Its density is high (9·8). It is strongly diamagnetic, *i.e.*, repelled by the poles of a magnet.

Bismuth is not affected by air at the ordinary temperature, but when heated it burns, producing a yellow smoke of its oxide $Bi_2O_3$. It burns in chlorine, forming the trichloride,

$$2Bi + 3Cl_2 = 2BiCl_3,$$

and also reacts with the other halogens and with sulphur. It is unattacked by ordinary dilute acids. Concentrated hydrochloric acid has little effect, but nitric acid and concentrated sulphuric acid attack it, forming the corresponding salts (*q.v.*).

Bismuth is a constituent of *fusible metals*, which are, as a rule, alloys of lead, tin, cadmium and bismuth. Wood's metal contains bismuth 4 parts, lead 2 parts, tin 1 part, cadmium 1 part, and melts at 65° C.

The high price of bismuth renders its use in solders very limited, but an alloy of bismuth, tin and lead is occasionally used where a very fusible solder is required.

**830. Atomic Weight.**—The atomic weight of bismuth is shown by Dulong and Petit's law and by the vapour densities of its volatile compounds (chloride, etc.) to be about 208. The most nearly accurate value is probably 209·00. Aston finds that ordinary bismuth contains no isotopes and has an atomic mass of 209.

**831. Bismuth Hydride $BiH_3$.**—This exceedingly unstable gas is evolved in very small quantities when a magnesium-bismuth alloy is dissolved in acids. Thus, if the alloy is placed in the apparatus for Marsh's test (Fig. 152) and treated with acids a faint ring of bismuth is obtained on the heated tube. Its existence was first demonstrated by using thorium C or radium C, which are radio-active isotopes of bismuth. These, alloyed with magnesium, evolved a radio-active gas, which was readily decomposed. A radio-active gas can, of course, be detected in much smaller quantity than that needed for the detection of any other type of substance. What little can be ascertained about bismuth hydride indicates that it is a very unstable gas, readily decomposed by the reagents which attack arsenic and antimony hydrides.

**832. Bismuth Oxides.**—Four oxides exist :—

| | |
|---|---|
| Bismuth monoxide . . . . | $BiO$ |
| Bismuth trioxide . . . . | $Bi_2O_3$ |
| Bismuth dioxide . . . . | $Bi_2O_4$ |
| Bismuth pentoxide . . . . | $Bi_2O_5$ |

**833. Bismuth Monoxide BiO** forms a black powder. It is obtained by the action of carbon monoxide on bismuth trioxide,

$$Bi_2O_3 + CO = 2BiO + CO_2,$$

or by heating bismuth oxalate. It has been thought to be a mixture of bismuth and bismuth trioxide.

**834. Bismuth Trioxide $Bi_2O_3$** is obtained by heating bismuth subnitrate or by burning the metal,

$$4BiONO_3 = 2Bi_2O_3 + 4NO_2 + O_2$$
$$4Bi + 3O_2 = 2Bi_2O_3.$$

It is a pale yellow fusible solid, which is readily reduced to the metal by heating with carbon or hydrogen. Carbon monoxide reduces it to the monoxide BiO. It has the ordinary properties of a basic oxide and is also feebly acidic, as is shown by its dissolving to a small extent in concentrated sodium hydroxide.

**835. Bismuth Dioxide $Bi_2O_4$** is made by the action of oxidising agents, such as chlorine on an alkaline suspension of bismuth trioxide.

It is a brown powder which, when heated, loses oxygen. With hydrochloric acid it gives chlorine and the trichloride, and with oxy-acids it gives oxygen and a salt of trivalent bismuth.

**836. Bismuth Pentoxide $Bi_2O_5$.**—If the process of oxidising bismuth trioxide with chlorine be carried on for a longer period, red potassium bismuthate $KBiO_3$ is precipitated. When this is treated with dilute nitric acid, metabismuthic acid $HBiO_3$ is formed and when this is dried bismuth pentoxide is formed as an unstable brown powder. When heated, and when treated with acids, it behaves like the tetroxide (*q.v.*). The bismuthates have been used as powerful oxidising agents.

A favourite method of estimating manganese in presence of much iron (as in steel) consists of dissolving the alloy in nitric acid and heating with sodium bismuthate. The manganese is oxidised to permanganate, and after filtration through asbestos in a Gooch crucible, is much diluted and titrated with ferrous ammonium sulphate.

**837. Bismuthyl Carbonate $(BiO)_2CO_3$** is the only carbonate formed by the elements of this family, and its existence illustrates the more metallic character of bismuth as compared with the other elements of the group.

**838. Bismuth Nitrate $Bi(NO_3)_3, 5H_2O$** is prepared by the action of nitric acid on bismuth, its oxide, or its carbonate. It is a white crystalline deliquescent salt and has the usual properties of a nitrate (§ 750). When mixed with much water the *subnitrate*, which has a considerable use in medicine, is formed.

$$Bi(NO_3)_3 + H_2O = BiONO_3 + 2HNO_3.$$

It was formerly employed as a face powder and stories are told of the faces of ladies seated by a coal fire becoming suddenly of a

tawny brown colour—hydrogen sulphide from the fire having converted the bismuth subnitrate into the black sulphide.

**839. Bismuth Sulphide $Bi_2S_3$** is precipitated when a current of hydrogen sulphide is passed through a solution of a bismuth salt. It is not acidic in character and thereby differs from antimony and arsenic sulphides. It is insoluble in alkaline sulphides.

**840. Bismuth Chloride $BiCl_3$** is formed when chlorine is passed over heated bismuth,

$$2Bi + 3Cl_2 = 2BiCl_3.$$

The ordinary methods for making chlorides may also be used.

It is a white solid, which melts at 227° C. and boils at 428° C. Its most interesting property is its ready formation of an insoluble basic salt (*cf.* $SbCl_3$, § 824).

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$

This property is used as a test for bismuth in qualitative analysis.

**841. Bismuth Oxychloride BiOCl** is prepared as above or by the reaction of dilute common salt solution with bismuth nitrate,

$$Bi(NO_3)_3 + 3NaCl + H_2O = BiOCl + 3NaNO_3 + 2HCl$$

It is used as a pigment under the name ' pearl white.'

**842. The Gradation of Properties in the Elements of Group V. (Typical Elements and B Sub-group).**—We note in this group a steady change in character as we pass from the typical non-metal nitrogen to the typical metal bismuth.

*The elements* of the group show this gradation well. Nitrogen shows no metallic appearance or chemical behaviour, nor does phosphorus, save in the one respect that black phosphorus conducts electricity. Arsenic in appearance resembles a metal; it conducts electricity as a metal does, but in its reactions with acids it resembles a non-metal. Antimony is, from the point of view of its physical properties, undoubtedly a metal, its brittleness alone linking it to the non-metals. Chemically, too, it resembles the metals except, perhaps, in its reaction with nitric acid to form an oxide. Bismuth is entirely metallic in all its characters.

*The hydrides* present also an interesting gradation. Ammonia is comparatively stable, but phosphine, arsine, stibine show a steadily diminishing stability, while bismuth hydride has but a fleeting existence. Again, ammonia is definitely basic, phosphine forms a few unstable salts and the rest form no inorganic salts, though organic arsonium and stibonium derivatives are known. No bismuthonium derivatives exist.

*The oxides* show the same gradation. Those of nitrogen and phosphorus are acidic or neutral. Arsenic trioxide shows a few basic characters, as in its reaction with hydrochloric acid. Antimony trioxide is amphoteric, both acidic and basic, while bismuth oxide is predominantly basic.

*The halides* again are of interest. The explosive nitrogen halides are certainly exceptional in type. The halides of phosphorus are definitely not salts—they are decomposed by water and certainly do not form a $P^{+++}$ ion. Arsenic chloride is easily hydrolysed, and the $As^{+++}$ ion may be formed from it in small quantity. Antimony and bismuth chlorides are definitely salts, and are not easily completely hydrolysed but form basic salts.

*Salts of Oxyacids* (sulphates, nitrates, etc.).—Nitrogen, phosphorus and arsenic resemble the non-metals in not forming salts with oxyacids; antimony forms a somewhat unstable sulphate, a nitrate, tartrate, etc., and bismuth behaves like a normal metal, except in its strong tendency to form basic salts.

We may, then, regard nitrogen and phosphorus as non-metals; arsenic as a non-metal with some metallic characters, antimony as a metal with some non-metallic characters, and bismuth as a metal. The term *metalloid* is often applied to arsenic and antimony to denote their intermediate position between the metals and non-metals.

## SUB-GROUP V. A.

### 843. Sub-Group V. A

The metals of sub-group V. A are :—

Vanadium.
Niobium (Columbium).
Tantalum.
Protoactinium.

Their atomic numbers and their electronic structures are given below :—

ELECTRONS OF QUANTUM NUMBER

| Atomic No. | Element. | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|
| 23 | Vanadium . | 2 | 8 | 8, 3 | 2 | | | |
| 41 | Niobium (Columbium) | 2 | 8 | 18 | 8, 4 | 1 | | |
| 73 | Tantalum . | 2 | 8 | 18 | 32 | 8, 3 | 2 | |
| 91 | Protoactinium | 2 | 8 | 18 | 32 | 18 | 8, 4 | 1 |

The elements of this group are characterised then by two incomplete outer groups of electrons containing 5 electrons in all. Their highest valency is in each case 5.

The elements of this group are of no great practical or scientific importance.

They are among the less common elements and are characterised by the following features.

The elements are metallic in appearance and physical properties. They are extremely hard and have very high melting points, *c.* 1,500–3,000° C. The elements are chemically of a metalloid or non-metallic character. They are fairly readily oxidised and are attacked by chlorine, but are comparatively resistant to the action of acids.

The elements form some lower oxides of valencies 2–4, but in their most stable compounds they are quinquevalent. They each form a pentoxide. The pentoxides of vanadium, niobium and tantalum are acidic in character and form salts analogous to the phosphates, but protoactinium pentoxide is feebly basic.

Their lower chlorides (valency $< 4$) are, if formed, very powerful reducing agents. The higher chloride $MCl_5$ is of the non-metallic type, being decomposed by water. Vanadium is exceptional in not forming a pentachloride.

## VANADIUM V, 50·95

**844. Occurrence and Preparation.**—Vanadium has been known since the early part of the nineteenth century. It does not occur native but is widely distributed in many rocks. Its chief ores are carnotite (potassium uranyl vanadate) and patronite, the latter a complex mixture of sulphides, The metal is obtained from the pentoxide by the aluminothermic process with mischmetall (§§ 480, 509),

$$3V_2O_5 + 10M = 6V + 5M_2O_3,$$

where M represents the various trivalent rare-earth metals in the mischmetall.

Ferrovanadium, the alloy of iron and vanadium, is made by reducing a mixture of iron oxide and vanadium oxide in the electric furnace.

Vanadium is also a common constituent of coals and petroleums. Italy, having no vanadium ores, obtained considerable quantities of the metal from the treatment of soot.

**845. Properties.**—Vanadium is a very hard and brittle grey-white metal. It melts at about 1,700° C. It is a fairly good conductor of electricity.

Vanadium burns in air or oxygen. If it oxidises slowly it successively forms the black trioxide, the blue tetroxide and the reddish-yellow pentoxide. Chlorine attacks it, forming the tetrachloride $VCl_4$.

Vanadium is not attacked by most acids. Hydrofluoric acid forms the fluoride, while concentrated nitric or sulphuric acid oxidises it to the pentoxide. Dilute nitric acid, however, forms the somewhat indefinite oxynitrate $VO(NO_3)_2$.

Vanadium finds a use in making vanadium steel. Steel containing a little of this metal is stronger than ordinary steel and finds a use for car-parts, etc., which are subjected to often-repeated shocks. Vanadium compounds have been used in medicine. They are very poisonous.

### Oxides of Vanadium

There are probably four oxides :—

| | |
|---|---|
| $V_2O_2$ | Vanadium dioxide. |
| $V_2O_3$ | Vanadium trioxide. |
| $V_2O_4$ | Vanadium tetroxide. |
| $V_2O_5$ | Vanadium pentoxide. |

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**846. Lower Oxides of Vanadium.**—*Vanadium dioxide* $V_2O_2$ is obtained by the action of a powerful reducing agent, such as potassium, on the higher oxides. It is a black powder. It dissolves in acids, forming lavender solutions of hypovanadous salts.

Vanadous oxide was mistaken for some time for the metal itself.

*Vanadous hydroxide* $V(OH)_2$, precipitated from the above, is one of the most powerful reducing agents in existence.

*Vanadium trioxide* $V_2O_3$ is obtained by reducing the pentoxide in a current of hydrogen. It is a black powder, which burns in air like tinder to the pentoxide or oxidises at lower temperature to the blue tetroxide. Acids do not attack it easily.

*Vanadium tetroxide* $V_2O_4$ is made by reducing the pentoxide with oxalic acid or sulphur dioxide,

$$V_2O_5 + H_2C_2O_4 = V_2O_4 + H_2O + 2CO_2.$$

It is readily oxidised to the pentoxide. The oxide is amphoteric, forming hypovanadates such as $Na_2V_4O_9$ with alkalis, and *vanadyl* salts as $VOCl_2$ with acids. These latter can also be made by reducing solutions of the pentoxide in acids.

**847. Vanadium Pentoxide $V_2O_5$** is made by strongly oxidising any vanadium compound. It is a yellowish-red powder, tasteless, but poisonous, which melts at about 660° C. and is not volatile at a red heat. It is sparingly soluble in water (1 : 1,000).

With strong acids vanadium pentoxide dissolves, forming a colloidal solution. With alkalis vanadates analogous to the phosphates are formed. Ortho-, meta- and pyrovanadates exist such as

$$Na_3VO_4,\ NaVO_3,\ Na_2V_2O_7.$$

Vanadium pentoxide is a rather weak oxidising agent.

**848. Oxysalts of Vanadium.**—Oxysalts derived from the lower oxides of vanadium are known, *e.g.* the sulphates $VSO_4$, $V_2(SO_4)_3$ and $VOSO_4$. The second forms a series of vanadium alums. No carbonate exists.

**849. Chlorides of Vanadium.**—The following chlorides are known :—

| | |
|---|---|
| $VCl_2$ | Green crystals. |
| $VCl_3$ | Peach-blossom coloured crystals. |
| $VCl_4$ | Brown liquid. |
| $VOCl_2$ | Blue. |
| $VOCl_3$ | Yellow liquid. |

The di- and trichloride are very powerful reducing agents, reducing copper and silver salts to the metals, bleaching indigo, etc.

Vanadium tetrachloride $VCl_4$, obtained by heating the metal in chlorine, is a heavy brown liquid, boiling at 154° C. It is decomposed by heat to the trichloride and chlorine.

Vanadium pentachloride is not known, but the metal is pentavalent in the oxychloride $VOCl_3$ a pale yellow liquid boiling at 127° C., produced by the action of chlorine on the trioxide. The pentafluoride $VF_5$ also exists.

## NIOBIUM Nb, 92·91 or COLUMBIUM Cb

**850. The Element Niobium.**—This rare element has been rediscovered a number of times since its first discovery in 1801, when it was termed columbium. Rose rediscovered it in 1844, and named it Niobium, a name it usually bears. The element has also been discovered on four other occasions as

*pelopium*, *dianium*, *neptunium*, and *ilmenium*, all of which turned out to be identical with niobium.

Niobium is always associated with tantalum, which it resembles strongly. Both *columbite* and *tantalite*, its chief minerals, are mixtures of iron and manganese niobates and tantalates. It is separated from the mineral by a similar method to that used for tantalum (§ 852).

The metal is obtained by reducing niobium pentoxide by the alumino-thermic method. Niobium is a hard white metal much resembling tantalum.

**851. Compounds of Niobium.**—It forms a pentoxide of acid character, $Nb_2O_5$, which forms well marked salts—niobates. The lower chlorides, $NbCl_2$, $NbCl_3$, are less powerful reducing agents than the corresponding vanadium compounds. A higher chloride, $NbCl_5$, is also known and much resembles tantalum pentachloride. The element has at present no uses.

## TANTALUM Ta, 181·4

**852. Occurrence and Extraction.**—Tantalum is chiefly found as the ore tantalite, ferrous tantalate, possibly $Fe_2Ta_4O_{12}$. Tantalite usually contains a variety of other elements, including manganese, titanium, niobium, silicon, etc.

To obtain pure tantalum pentoxide, tantalite may be fused with potassium hydrogen sulphate. The mass is extracted with water, and iron, manganese, etc., go into solution as sulphates. Tin and tungsten are removed from the residue by digestion with ammonium sulphide. The residue contains tantalum pentoxide, niobium pentoxide, titanium dioxide and silica. These are all dissolved in hydrofluoric acid and potassium fluoride added. Potassium tantalifluoride, niobifluoride, titanifluoride and silicofluoride are all formed, but the first is readily separated by crystallisation.

This may be heated with concentrated sulphuric acid, yielding tantalum pentoxide $Ta_2O_5$,

$$Fe_2Ta_4O_{12} + 4KHSO_4 = 2FeSO_4 + 2Ta_2O_5 + 2H_2O + 2K_2SO_4$$

$$Ta_2O_5 + 5H_2F_2 = 2TaF_5 + 5H_2O$$

$$2KF + TaF_5 = K_2TaF_7$$

$$2K_2TaF_7 + 4H_2SO_4 + 5H_2O = 4KHSO_4 + 7H_2F_2 + Ta_2O_5.$$

To obtain metallic tantalum the double fluoride of tantalum and potassium, $K_2TaF_7$, obtained as above, may be heated in an evacuated tube with sodium or potassium. Powdered tantalum is thus obtained,

$$K_2TaF_7 + 5Na = Ta + 2KF + 5NaF,$$

which is compressed and fused in a vacuum electric furnace.

**853. Properties.**—Tantalum is a white-grey metal of very high melting point, *c.* 2,800° C. The worked metal is extraordinarily tough and hard, and when the surface is slightly oxidised it can hardly be attacked with the diamond drill. Tantalum wire was formerly used in electric glow-lamps in the same manner as tungsten.

Its use in filaments for electrical lamps depends on its very high melting point, its high resistance and its great strength. The wire used is so fine that 45,000 lamps can be made from 1 kilo of tantalum. It has been superseded for this purpose by tungsten.

Tantalum is readily oxidised at a red heat, and it burns in oxygen at about

600° C. It also burns in chlorine. The red-hot metal decomposes steam. At lower temperatures the metal is very unreactive, for neither water nor acids have any effect upon it. It has been used for dental and surgical instruments, which do not rust and are also of great mechanical strength.

**854. Oxides of Tantalum.**—One lower oxide exists but the only oxide of importance is tantalum pentoxide $Ta_2O_5$.

*Tantalum pentoxide* $Ta_2O_5$ is found when tantalum burns in air, but is usually made as described above in § 852. It is a dense white powder infusible at 1,600° C. It is not reduced by hydrogen nor is it attacked by acids.

*Tantalum hydroxide* (*tantalic acid*) is prepared by the action of tantalum pentachloride on water,

$$TaCl_5 + 5H_2O = Ta(OH)_5 + 5HCl,$$

when dried it has the formula $HTaO_3$.

Tantalic acid is a white powder, which is not attacked by acids but which is easily soluble in alkalis, forming *tantalates*.

**855. Chlorides of Tantalum.**—The lower chlorides, $TaCl_2$, $TaCl_3$, $TaCl_4$ are reducing agents. Tantalum pentachloride, made by the action of chlorine on the metal or a mixture of the pentoxide and carbon, forms white crystals which melt at *c.* 210° C. and boil at 242° C. It hisses when dropped into water, forming tantalic acid.

Tantalum does not form any oxy-salts except a doubtful sulphate.

## PROTOACTINIUM Pa, 231

This element is discussed with the other radio-active elements in Chapter XXVI. Its properties are still under investigation, some 0·5 gm. having been prepared from radium residues. It resembles tantalum except in so far that its pentoxide is basic in character, not acidic like that of the latter metal. It should be noted that this is to be expected in view of the fact that thorium is more basic than hafnium and uranium than tungsten (*v.* also § 1270).

# CHAPTER XIX

## OXYGEN AND OZONE

**856. History.**—The discovery of oxygen represents one of the fundamental advances in the knowledge of chemistry. It was for a great many years supposed that air was an element or at least a simple substance. The researches of Boyle and Hooke, in the seventeenth century, proved that a part of the air was concerned in respiration and combustion. Hooke and Mayow, in the seventeenth century, came near the truth when they assumed that air contained a substance which was responsible for combustion, the calcination of metals and respiration. This substance they correctly supposed to be present in saltpetre, and Mayow termed it *spiritus nitro-aëreus*. If he had isolated the gas he would be called the discoverer of oxygen. His early death and the development of the phlogiston theory caused his researches to be neglected and the next step was the discovery of oxygen itself by Scheele (in 1771–1773). Priestley, in 1774, discovered the gas independently and named it "dephlogisticated air." Priestley heated mercuric oxide, confined over water, by means of a burning-glass. Both Scheele and Priestley recognised that the gas was contained in the air, but were so possessed by the doctrine of phlogiston that the real importance of the discovery escaped them.

It remained for Lavoisier to demonstrate the real importance of oxygen and to show, what Priestley and Scheele did not realise, *that combustion, calcination of metals, and respiration, were processes of combination with oxygen.*

Lavoisier, in 1772, hit on the essential fact that when metals and some other substances underwent combustion or calcination their weight increased *as a result of combination with air*. He was evidently not clear as to what part of the air was concerned in this process until he heard of Priestley's discovery, which opened his eyes to the true state of affairs. Regrettably, Lavoisier made no satisfactory acknowledgment of what he owed to Priestley, but rather attempted to imply that he had discovered the gas himself independently of Priestley. None the less, Lavoisier deserves the fullest credit for his brilliant investigation of the true nature and properties of the gas. Of his many experiments on the relationship of oxygen and air, the most famous and convincing is described below.



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Lavoisier placed some mercury in a retort with a long neck, bent so as to pass under the surface of mercury contained in a trough and to rise up into the air confined in a bell jar over this mercury (Fig. 154). At the beginning of the experiment the mercury level was marked and the mercury was then heated by a charcoal furnace to a little below its boiling point. He saw that after some days red particles collected on the surface, and after some time ceased to increase in quantity. He then let the fire out and ascertained that, making due allowance for changes of pressure, about a sixth of the air had disappeared. The remaining air supported neither combustion nor life. Lavoisier termed this gas (nitrogen) 'azote.' He collected the red solid which had formed in the retort and heated it. He obtained from it, within the rather wide limits of his experimental error, *just as much oxygen as the air had lost*, and on mixing this oxygen with azote, air was reproduced which behaved in

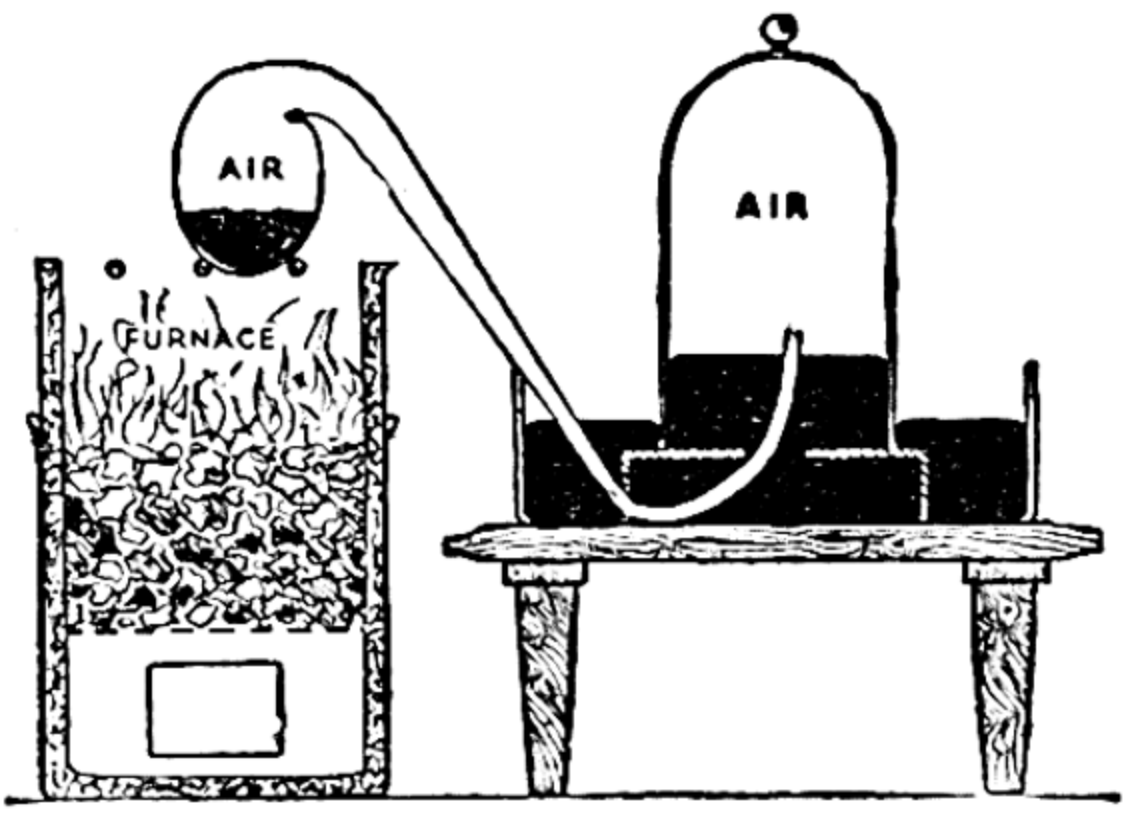


FIG. 154.—Lavoisier's experiment.

every way like atmospheric air. This experiment showed conclusively that air was a mixture of oxygen and azote or nitrogen.

**857. Occurrence.**—Oxygen is the most widely distributed and the commonest of elements. Not only does it form about one-fifth of the air and eight-ninths of water by weight, but it also forms a large part of nearly all rocks. Thus calcium carbonate (chalk, limestone, etc.) contains 48 per cent., and silica (flint, quartz), 53·7 per cent. of oxygen by weight.

The almost exact constancy of the proportion of oxygen in the air will be understood from a study of the carbon dioxide cycle (§ 561).

**858. Preparation and Manufacture of Oxygen.**—Oxygen is prepared either by separation from the atmosphere or by decomposition of oxygen-containing compounds, notably oxides and oxy-salts.

**859. Oxygen from the Atmosphere.**—The air is the most obvious and cheapest source of oxygen and numerous methods of obtaining oxygen from it have been devised. These include the only commercial method of preparation, *i.e.*, the fractional evaporation of liquid air, and various methods based on the absorption of oxygen by a substance and the subsequent decomposition of the compound formed.

The air liquefaction process is fully described under the heading of nitrogen (§ 678). It yields very pure oxygen, containing only a trace of nitrogen as impurity.

*Brin's process*, now obsolete, was conducted by causing air to combine with heated barium oxide, forming barium peroxide according to the equation

$$2BaO + O_2 \rightleftharpoons 2BaO_2.$$

It follows from the fact that the formation of barium peroxide is accompanied by a large decrease of total volume that an increase of oxygen pressure will cause the equilibrium to shift so that the peroxide is formed, while a decrease of pressure will cause the peroxide to be decomposed. Barium oxide was heated to 700° C., and first exposed to air at 10 lb. sq. inch pressure. The pressure was after seven minutes decreased to 4 inches of mercury and the oxygen previously absorbed was once more evolved.

Calcium plumbate, obtained by heating lead oxide with chalk, has been used in the same way as barium oxide. It reacts with oxygen of the air,

$$2CaPbO_3 \rightleftharpoons 2CaO + 2PbO + O_2.$$

Lavoisier's famous experiment (§ 856) provides a method—historically of interest, but of no practical importance—of obtaining oxygen from the air by the reaction

$$2HgO \rightleftharpoons 2Hg + O_2.$$

**860. Oxygen from Oxides.**—(1) The majority of oxides are not decomposed by heat. The basic oxides of the more 'noble' metals, including the platinum metals, gold, silver and mercury, are, however, decomposed in this way,

$$2Ag_2O = 4Ag + O_2.$$

These methods are not practically important. Most higher oxides and peroxides are decomposed in this way. Thus manganese dioxide, lead dioxide, red lead, chromium trioxide, and the peroxides of all metals except the alkali metals are decomposed by heat to lower oxides and oxygen. The preparation of oxygen by heating manganese dioxide to a strong red heat was at one time commercially exploited. The other oxides are decomposed at lower temperatures.

$$\begin{aligned} 3MnO_2 &= Mn_3O_4 + O_2 \\ 2PbO_2 &= 2PbO + O_2 \\ 2Pb_3O_4 &= 6PbO + O_2 \\ 4CrO_3 &= 2Cr_2O_3 + 3O_2 \\ 2ZnO_2 &= 2ZnO + O_2. \end{aligned}$$

Hydrogen peroxide is readily decomposed by heat, but its oxygen is more satisfactorily utilised by its reaction with potassium permanganate (p. 599).

(2) Water may be decomposed by electrolysis (§ 181). The process is occasionally used commercially. In the laboratory the method is used where very pure oxygen is required. The electrolysis of barium or sodium hydroxide solution yields a purer gas than the electrolysis of dilute sulphuric acid. The process is illustrated in Fig. 155. In this form of apparatus barium hydroxide solution is electrolysed, using nickel sheet electrodes. Very pure oxygen for the determination of the atomic weight of hydrogen was prepared by Noyes in a similar manner and then further purified. His method is described in § 69.

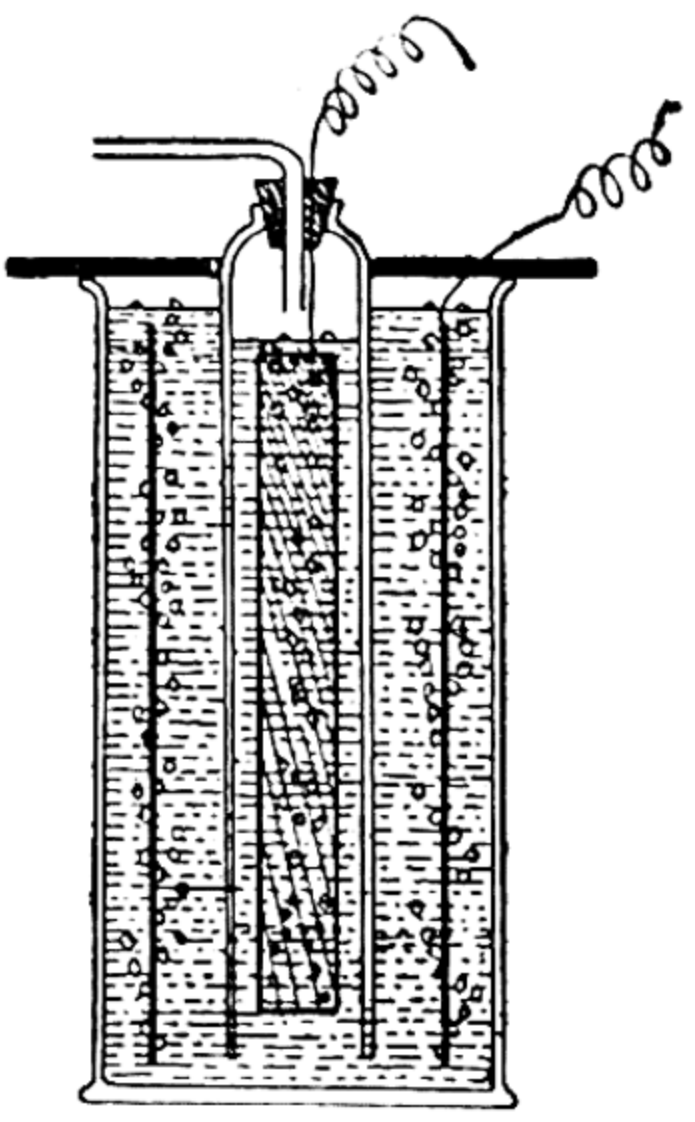

Fig. 155.—Preparation of oxygen by electrolysis.

(3) The peroxides of alkali metals may be decomposed by the action of water. If water be allowed to drop on solid sodium peroxide, oxygen is steadily evolved,

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2,.$$

Sodium peroxide made into cubes with a little copper sulphate (which acts catalytically) is sold for this purpose.

(4) Certain higher oxides are decomposed by acids, yielding salts of lower oxides and free oxygen. Thus manganese dioxide, lead dioxide, chromium trioxide, when heated with sulphuric acid, yield oxygen,

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$$
$$4CrO_3 + 6H_2SO_4 = 2Cr_2(SO_4)_3 + 6H_2O + 3O_2.$$

**861. Oxygen from Oxy-salts.**—Many oxy-salts, such as chlorates, permanganates, nitrates, decompose when heated. Of these potassium chlorate is by far the most convenient.

(5) Oxygen is usually prepared in the laboratory by the action of heat on potassium chlorate. The pure salt melts when heated and gives off oxygen rapidly at 370°–380° C. At this temperature two reactions take place,

$$(1)\ 2KClO_3 = 2KCl + 3O_2.$$
$$(2)\ 4KClO_3 = KCl + 3KClO_4.$$

Above 400° C. the perchlorate formed in the second reaction also decomposes,

$$(3)\ KClO_4 = KCl + 2O_2,$$

the final products of strong heating being potassium chloride and oxygen.

The reaction requires rather too high a temperature for convenience, and consequently it is usual to mix manganese dioxide to the end that the reaction may take place at a lower temperature and more smoothly than is the case with the chlorate alone.

The exact mode of action of the manganese dioxide is still in doubt, but the theory of Macleod seems the most probable. He supposes that potassium permanganate is alternately formed and decomposed according to the equation

$$(a)\ 2MnO_2 + 2KClO_3 = 2KMnO_4 + Cl_2 + O_2,$$
$$(b)\ 2KMnO_4 = K_2MnO_4 + MnO_2 + O_2,$$
$$(c)\ K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2.$$

This theory explains the facts that a trace of chlorine is found in the gas,

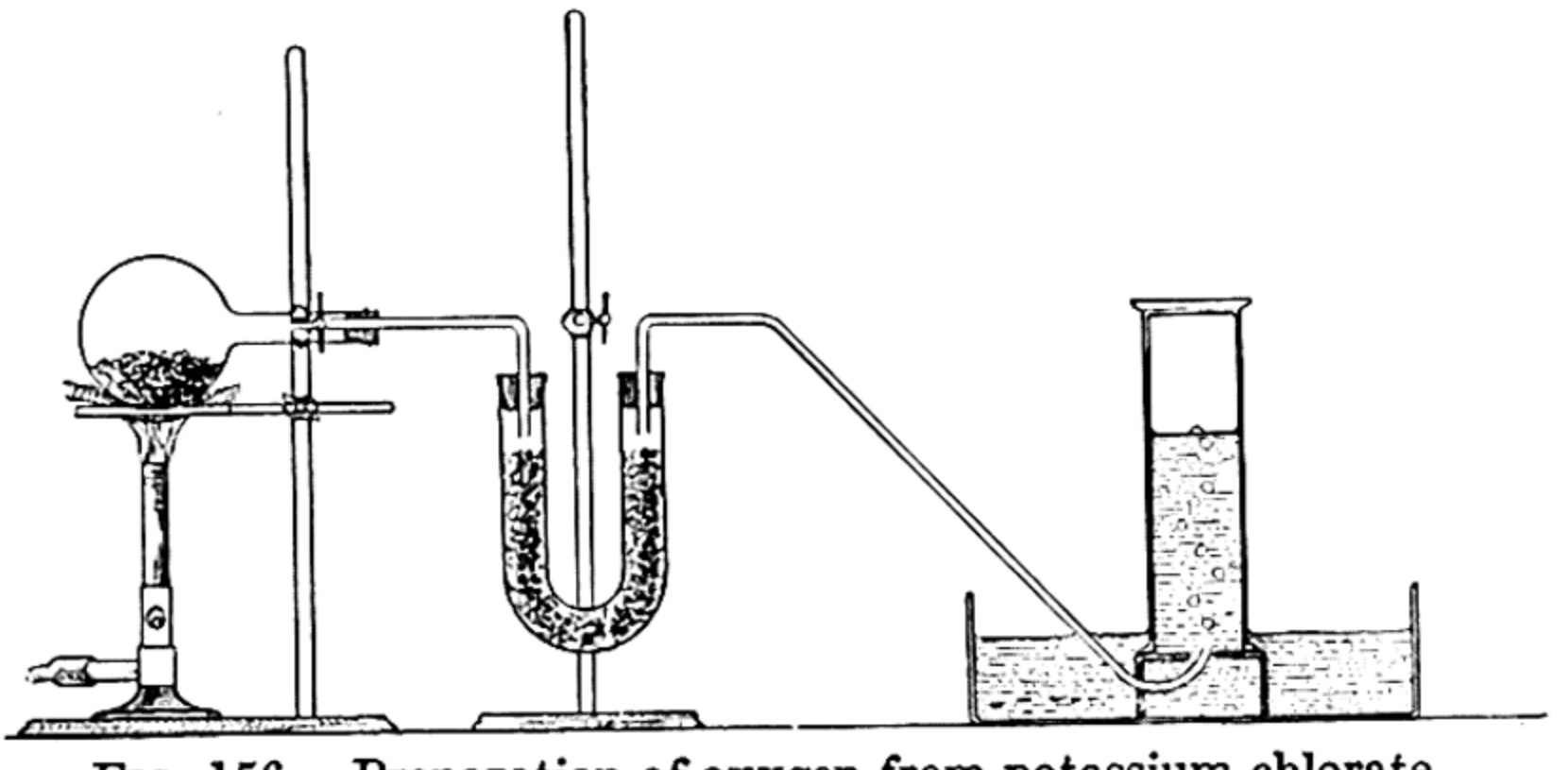

FIG. 156.—Preparation of oxygen from potassium chlorate.

and that the residual chloride is distinctly pink, this colour being attributed to permanganate.

It has been supposed that a higher oxide of manganese is alternately formed and decomposed.

$$(a)\ 2MnO_2 + KClO_3 = Mn_2O_7 + KCl.$$
$$(b)\ 2Mn_2O_7 = 4MnO_2 + 3O_2.$$

A third theory supposes that the action of the dioxide is to provide nuclei from which the oxygen, held in supersaturated solution by the chlorate, may be evolved. This latter theory fails to explain the specific effect of metallic oxides as distinguished from other powders.

It is of interest that nickel oxide and ferric oxide are catalysts as efficient as manganese dioxide.

The apparatus used is shown in the figure.

The gas obtained may contain carbon dioxide, moisture and chlorine, the first being derived from impurities in the manganese

dioxide. They may be removed by passing the gas first through a soda-lime tube, then through sulphuric acid.

(6) Potassium nitrate yields oxygen when heated to a low red heat and leaves a residue of nitrite. The temperature is too high for the use of soft glass vessels.

$$2KNO_3 = 2KNO_2 + O_2.$$

Potassium dichromate is decomposed only at a white heat, but potassium permanganate decomposes at 240° C., giving the manganate, manganese dioxide and oxygen,

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

(7) Potassium permanganate and hydrogen peroxide react in presence of sulphuric acid, forming oxygen, manganous sulphate, potassium sulphate and water. The acidified permanganate may be allowed to drop from a tap-funnel into 10-volume peroxide solution. The gas so obtained is very nearly pure.

$$5H_2O_2 + 2KMnO_4 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Potassium dichromate (§ 995) may replace the permanganate. Many other oxidising agents react with hydrogen peroxide in a similar way (p. 253).

(8) The action of concentrated sulphuric acid on certain oxysalts yields oxygen. The permanganates react with explosive violence, owing to the formation of the unstable oxide $Mn_2O_7$, but the dichromates give a steady stream of gas,

$$2K_2Cr_2O_7 + 10H_2SO_4 = 4KHSO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2.$$

(9) Bleaching powder solution readily decomposes in presence of a cobalt salt, yielding oxygen,

$$2CaOCl_2 = 2CaCl_2 + O_2.$$

The mechanism of the catalytic action of the cobalt is discussed on p. 126.

(10) Green plants decompose carbon dioxide under the action of light, building up starch and liberating oxygen. The presence of the green pigment chlorophyll is necessary. The process is symbolised as

$$6nCO_2 + 5nH_2O = (C_6H_{10}O_5)_n + 6nO_2.$$

Doubtless the reaction takes place in several stages. The process transforms the carbon dioxide exhaled by animals and evolved by combustion back to oxygen and so keeps the composition of the air approximately constant. Colourless plants, such as fungi, if these may be called plants, and certain parasitic plants, such as dodder, are unable to build up food in this way, but must take it ready-made from decaying organic matter or a living host.

**862. Formula and Atomic Weight of Oxygen.**—The atomic weight of oxygen is taken as the chemical standard, 16·000.

The physical standard is the atomic weight of the $O^{16}$ isotope taken as 16·000. Traces of isotopes $O^{17}$ and $O^{18}$ are contained in the gas, and this occasions a difference of about one part in ten thousand between these standards (§ 67).

Compounds of the $O^{18}$ isotope are now becoming available, *e.g.*, $H_2O^{18}$.

That the formula of oxygen is $O_2$ is shown by the fact that one volume of oxygen can be made to form two volumes of steam, carbon monoxide, or nitric oxide. One molecule of oxygen therefore yields two molecules of these gases and must contain *at least* two atoms. That it does not contain more than two atoms is shown by the fact that one volume of oxygen never produces *more* than two volumes of a gaseous oxide. The density of the gas and the ratio of its specific heats, $C_p/C_v = 1{\cdot}4$ at 15° C., afford additional evidence.

*Physical Properties.*—Gaseous oxygen is a colourless gas without taste or smell. The physiological importance of the gas is discussed under the heading of its chemical properties.

Oxygen may be liquefied by the methods indicated in § 678, to a very pale blue liquid, boiling at − 183° C. under atmospheric pressure. By cooling with liquid hydrogen this may be solidified to a bluish-white solid, melting at − 219° C. Liquid oxygen is perceptibly magnetic. Gaseous oxygen has a density of 15·87 ($H_2 = 1$). It is therefore somewhat heavier than air.

Oxygen is sparingly soluble in water, about 3 volumes of the gas dissolving in 100 of water at 20° C. This solubility, though slight, is of high importance, for it is the presence of this free oxygen in water that enables fishes, etc., to respire. Oxygen dissolves in molten silver (§ 302).

**863. Chemical Properties.**—Oxygen is slightly dissociated when heated to very high temperatures.

When subjected to the silent electric discharge it forms ozone, $O_3$ (§ 875).

Oxygen combines directly with all the elements except the inert gases, the halogens, silver, gold and some of the platinum metals. One or more of the oxides are in every case formed :

$$2Cu + O_2 = 2CuO + 37{\cdot}7 \text{ Cals.}$$
$$S + O_2 = SO_2 + 69{\cdot}3 \text{ Cals.}$$
$$4P + 5O_2 = P_4O_{10} + 730{\cdot}6 \text{ Cals.}$$

In some cases the combination is accompanied by *combustion* and the element burns in oxygen. This takes place when the heat of combination evolved is sufficiently great and sufficiently rapidly

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produced to keep the element at a temperature at which its combination with oxygen can continue. Thus copper will not burn in oxygen although it is oxidised, for the reaction with the gas is slow and evolves comparatively little heat. In general, the elements burn most readily in oxygen when their heat of combustion is great (*e.g.*, sodium, magnesium); when they expose a large surface (charcoal, finely divided iron, 'pyrophoric' lead, etc.), or are gaseous or volatile (sulphur, hydrogen, etc.). The elements which combine with oxygen but do not burn in it have either a small or negative heat of reaction (nitrogen, mercury) or are non-volatile, exposing a small surface (diamond, graphite), or become coated with an impervious layer of oxide (nickel, chromium).

The subject of combustion has been dealt with in Chapter XV. The chemical character of the oxides produced is discussed in §§ 867–873.

A few substances—elements or compounds—react with oxygen in the cold. Among these we may note white phosphorus, which reacts with the gas, forming the trioxide,

$$4P + 3O_2 = 2P_2O_3,$$

moist ferrous hydroxide which forms the ferric compound,

$$2Fe(OH)_2 + H_2O + O = 2Fe(OH)_3,$$

and nitric oxide which forms the brown gas, nitrogen peroxide,

$$2NO + O_2 = 2NO_2.$$

Manganous hydroxide (§ 1110), hydrogen sulphide, ammonium sulphide, and among less important compounds, phosphine, thiophosphoryl fluoride $PSF_3$, chromous, vanadous and titanous salts, and certain organic compounds (*e.g.*, benzaldehyde, indigo white) also react in the cold with oxygen.

Sodium pyrogallate very readily absorbs free oxygen, forming dark-coloured oxidation products.

Many compounds react with oxygen when heated in it. In general, any substance will burn in oxygen if all the elements contained in it will do the same (*e.g.*, $PH_3$, $CS_2$, $SiH_4$, $P_4S_3$) and a great many other substances burn in oxygen which do not fulfil these conditions. Mixtures of combustible gases and oxygen explode when heated if the proportions of the gases are within certain limits.

The reactions of particular elements and compounds with oxygen are discussed under their respective headings.

**864. Oxygen and Respiration.**—All living organisms expend energy in building up tissues and in performing internal and external work.

This energy is derived from the oxidation of certain compounds. The oxygen required for this purpose is supplied by the process of respiration. In the simplest animals mere external contact with free oxygen, usually dissolved in water, gives a sufficient supply, but larger creatures with a greater ratio of volume to surface require a more complex system of supply. Respiration consists of the transfer of oxygen from the air to the part of the body where it is required. In the higher animals this is accomplished by the circulation of blood, first through the lungs or gills, and then through the tissues. The lung of a man is a complex structure, which may be visualised as a system of air-passages connected like the twigs and branches of a tree, and terminating in minute air-cavities, the walls of which are a close network of minute blood vessels separated from the air by an exceedingly delicate membrane. Through these capillary blood-vessels pass some 5 to 25 litres of blood every minute, while the lungs hold some 3 litres of air which is continuously being changed by the process of breathing.

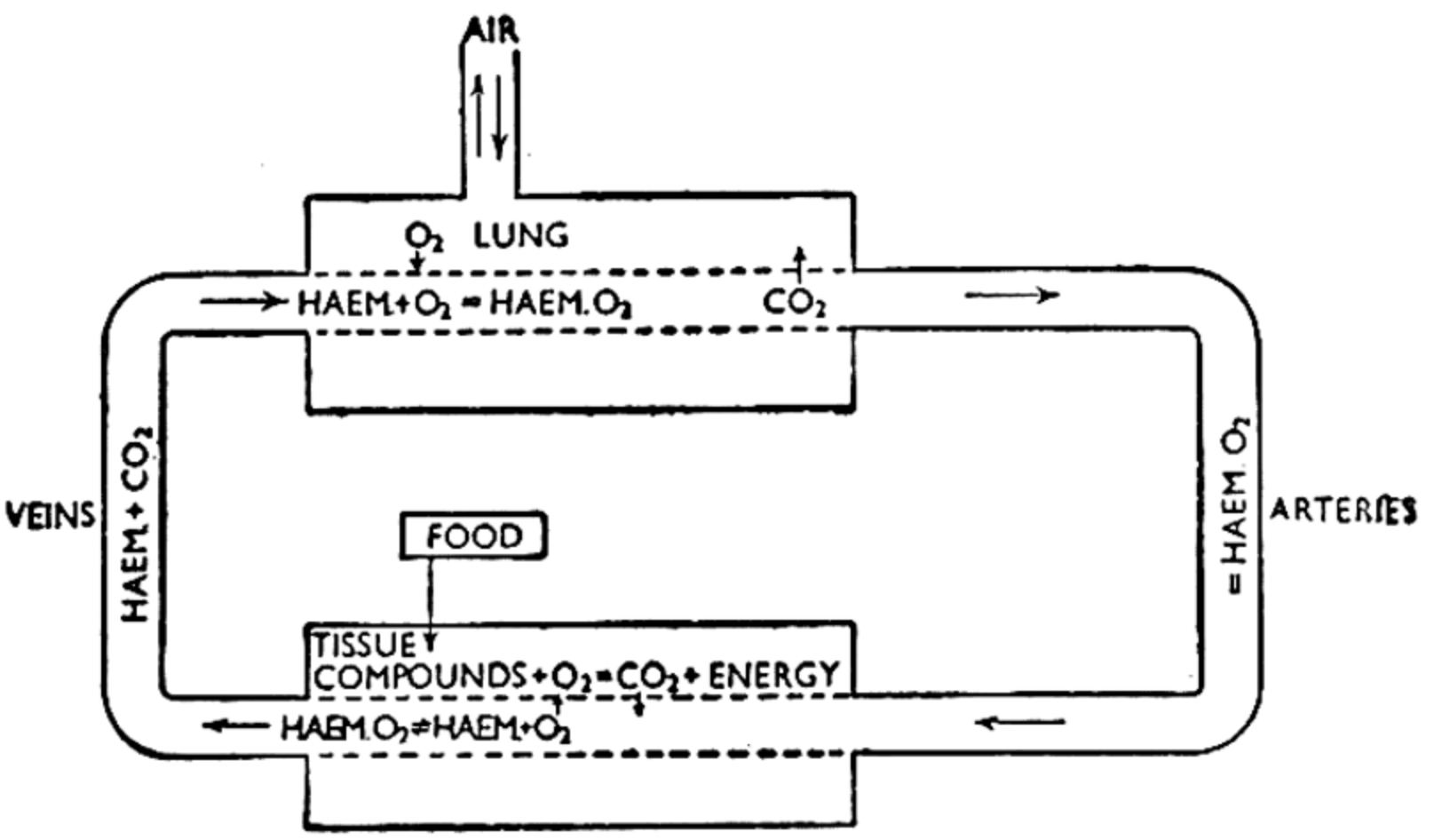



FIG. 157.—Oxygen and respiration: HAEM. = hæmoglobin; HAEM.$O_2$ = oxyhæmoglobin.

The blood consists of a clear *plasma* which is a solution of various proteins in which float red corpuscles containing *hæmoglobin*, a complex purple organic compound containing iron, etc. Its structural formula is not known, though a general idea of its constitution has been gained. Hæmoglobin and oxygen are in equilibrium with the bright red compound, oxy-hæmoglobin. In the lungs there is a fairly high concentration of oxygen and so the blood leaving the lungs contains a high proportion of oxy-hæmoglobin. This is carried from the lungs to all parts of the body. Every tissue in the body uses up oxygen in quantity varying from 3 to 10 milligrams per gram of tissue per minute. In these tissues, accordingly, there is a

smaller concentration of oxygen than is in equilibrium with oxy-hæmoglobin, which decomposes, liberating oxygen, and returns as hæmoglobin to the lungs *via* the veins. The use of the oxygen to the body is to oxidise various carbon compounds to carbon dioxide, thereby providing the energy needed for warming the body and doing muscular and chemical work. The carbon dioxide dissolves in the plasma of the blood, and so returns to the lungs, where it is evolved.

The diagram (Fig. 157) gives some idea of the process.

The rate of breathing is delicately regulated by the carbon dioxide content of the blood acting on the respiratory nervous centre in the brain. Thus exercise requires oxidation to provide its energy: carbon dioxide is produced in greater quantity; the blood becomes slightly more acidic; and the respiratory centre responds by causing deep breathing which changes the air in the lung more often, and so washes out the carbon dioxide from the blood. The blood regulates the rate of breathing by its carbon dioxide content, not by its oxygen content. Hence the rate of breathing will not adjust itself to an atmosphere containing very little oxygen or very much oxygen. The first causes blueness of the skin, weakness, and finally death, while the latter causes high temperatures and finally also death. If the lung is defective, as in pneumonia, a higher concentration of oxygen (*c.* 50 per cent.) is valuable, but pure oxygen is always poisonous. For the normal lung one cannot improve on natural air, to the use of which our bodies have adapted themselves for tens of millions of years. The exact means by which the oxygen passes through the capillary wall is not certain, but is probably a process of diffusion.

**864a. Atomic Oxygen O** is produced to the extent of about 20 per cent. when oxygen is subjected to an electric discharge (0·25 ampere, 4,000 volts) at a pressure of about 1 mm. It reacts in the cold with hydrogen. It oxidises carbon monoxide and methane. Methyl alcohol, benzene, acetylene and cyanogen are also oxidised by it to water and oxides of carbon, a bright glow being produced.

Halogen hydrides (except $H_2F_2$) and ammonia are also oxidised, and even the very stable carbon tetrachloride is oxidised to carbonyl chloride and chlorine.

**865. Uses of Oxygen.**—Oxygen is used in medical practice for administration to persons suffering from difficulties in respiration, as in lung affections such as pneumonia. A mixture of equal parts of oxygen and air is the most suitable. It is also used mixed with carbon dioxide in artificial respiration; and it is mixed with nitrous oxide or ethylene when these gases are administered as anæsthetics.

Oxygen is much used in the oxyacetylene blow-pipe. If an excess

of acetylene is used a flame intensely hot and yet not oxidising in character is obtained, which is peculiarly suitable for welding. Iron and steel are cut by heating the metal till it begins to burn and directing a jet of oxygen on to the heated spot. The metal burns brilliantly and melts like wax at the spot heated. In this way very thick steel plates may be easily cut.

The oxyhydrogen flame has been used in the *limelight* (§ 357), and furnaces blown with a mixture of oxygen and air are very convenient for high-temperature laboratory work.

**866. Detection and Estimation.**—Free oxygen, if more than about 30 per cent. be present in the mixture tested, relights a feebly glowing splinter. Nitrous oxide relights a strongly glowing splinter, but is easily distinguished from oxygen by any of the other tests.

Oxygen is completely absorbed by potassium pyrogallate solution or by phosphorus standing over water, and it is estimated by absorption with the former reagent in some form of gas apparatus. The estimation of oxygen in air is carried out by this method (§ 685).

## OXIDES

**867. Types of Oxide.**—The compounds of oxygen with the elements are of great importance and fall into certain well-marked types.

They are ordinarily classified under six headings, namely :—

(i.) Neutral oxides.
(ii.) Acidic oxides.
(iii.) Basic oxides.
(iv.) Amphoteric oxides.
(v.) Peroxides.
(vi.) Compound oxides.

**868.** (i.) **Neutral oxides** are those which react neither with acids nor with bases to form salts. They include water, carbon monoxide, nitrous and nitric oxides. They have few other common properties.

**869.** (ii.) **Acidic oxides** are those which react with bases to form salts. We may take carbon dioxide as an example, *e.g.*,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

If soluble in water they combine with it, forming an acid. Thus sulphur trioxide and water give sulphuric acid,

$$SO_3 + H_2O = H_2SO_4.$$

It is not usual to include under this heading the amphoteric oxides which possess the properties both of acidic and of basic oxides.

Among the acidic oxides we may note boron trioxide, carbon dioxide, silica, stannic oxide, titanium dioxide, nitrogen trioxide, and pentoxide, phosphorus trioxide and pentoxide, the pentoxides of arsenic and antimony, the oxides of sulphur, selenium and tellurium, chromium trioxide, manganese heptoxide, and the oxides of the halogens. From this list it will appear that the oxides of the non-metals are usually acidic in character.

**870.** (iii.) **Basic oxides** are those which react with acids to form salts and water. If they dissolve in water they form a soluble hydroxide or alkali, *e.g.*,

$$Na_2O + H_2O = 2NaOH.$$

If we exclude amphoteric oxides we may note among the most important basic oxides the lower oxides of the alkali metals and of the alkaline earths, cuprous and cupric oxides, silver, gold, iron, nickel and cobalt oxides.

Basic oxides are always oxides of metals, never of non-metals or metalloids.[1]

**871.** (iv.) **Amphoteric oxides** have to some extent the properties of both acidic oxides and basic oxides. Thus aluminium oxide forms, with acids, aluminium salts,

$$Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O,$$

but with alkalis, aluminates,

$$2KOH + Al_2O_3 = 2KAlO_2 + H_2O.$$

Amphoteric oxides are not, as a rule, equally strongly basic and acidic. Thus antimony trioxide is predominantly acidic, while zinc oxide is predominantly basic. The amphoteric oxides include the oxides of zinc, aluminium, zirconium, stannous oxide, lead monoxide, the trioxides of arsenic, antimony and bismuth, manganese and chromium sesquioxides.

**872.** (v.) **Peroxides,** when treated with dilute acids, yield hydrogen peroxide,

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

The peroxides of the alkali metals, alkaline earths and zinc are the most stable, but most metals form a peroxide.

They are probably salts of hydrogen peroxide, of structures such as

$$Na^+[O - O]^=Na^+ \qquad Ba^{++}[O - O]^=$$

The name of peroxide is incorrectly applied to such oxides as $PbO_2$ and $MnO_2$, which are basic or amphoteric oxides with unstable salts. These react with acids with difficulty and produce the salt

[1] GeO is perhaps an exception.

of a lower oxide together with oxygen (or chlorine if hydrochloric acid is used). They do not yield hydrogen peroxide,

$$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2.$$
$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

The oxygen atoms in these are probably not chemically combined with each other and their formulæ may be,

$$O = Pb = O, \quad O = Mn = O.$$

**873. (vi.) Compound Oxides** behave like a compound of two oxides, though they may not actually be so. Thus triferric tetroxide $Fe_3O_4$ behaves like a compound of ferrous and ferric oxides $FeO.Fe_2O_3$, and forms ferrous and ferric salts with acids,

$$Fe_3O_4 + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O.$$

Under this heading come triferric tetroxide, $Fe_3O_4$, red lead, $Pb_3O_4$, brown oxide of manganese, $Mn_3O_4$, and possibly the 'mixed anhydrides,' nitrogen peroxide and phosphorus tetroxide, which behave in some respects as if they were compounds $N_2O_3.N_2O_5$, $P_2O_3.P_2O_5$.

The following table may be found useful. The rarest elements are excluded :—

| Elements which form an Acidic Oxide but no Amphoteric or Basic Oxide. | Elements which form an Acidic Oxide as well as an Oxide of Basic or Amphoteric Type. | Elements which form an Amphoteric Oxide but not an Acidic Oxide. | Elements which form Basic Oxides but no Amphoteric or Acidic Oxides. |
|---|---|---|---|
| Chlorine. | Arsenic. | Tin. | Iron. |
| Bromine. | Antimony. | Lead. | Cobalt. |
| Iodine. | Bismuth. | Aluminium. | Nickel. |
| Sulphur. | Chromium. | Gold. | Platinum. |
| Selenium. | Molybdenum. | Zinc. | Thorium. |
| Tellurium. | Tungsten. | Uranium. | Cadmium. |
| Nitrogen. | Manganese. | Zirconium. | Mercury. |
| Phosphorus. | | | Copper. |
| Carbon. | | | Silver. |
| Silicon. | | | The alkaline earth metals. |
| Titanium. | | | The alkali metals. |
| Boron. | | | |

## OZONE

**874. Historical.**—The smell associated with an electrical discharge was noticed by Van Marum in 1785, and in 1840 Schönbein attributed this to a new gas, ozone (Greek ὄζω, *ozo*, I smell). The formula $O_3$ was established by Soret in 1866. It was formerly thought that air

contained appreciable quantities of ozone, but the proportion present appears to be of the order of 1 part in a hundred million of air.

**875. Preparation.**—Ozone is formed from oxygen with considerable absorption of energy,

$$3O_2 \rightleftharpoons 2O_3 - 69 \text{ Cal.}$$

It should therefore be formed in large quantities at extremely high temperatures above 3,000° C. There is evidence that this is the case, but it is clear that unless the heated oxygen were instantly removed from the sphere of reaction and cooled, all the ozone formed would decompose once more during cooling.

Actually, ozone is usually made by the action of the silent electrical discharge on air or oxygen. Sparking should not occur, for the heat so produced decomposes most of the ozone. The apparatus illustrated is of two types. Both patterns cause oxygen to flow between two or more surfaces kept charged to an extent which does not cause sparking. The simple type (Fig. 158) may

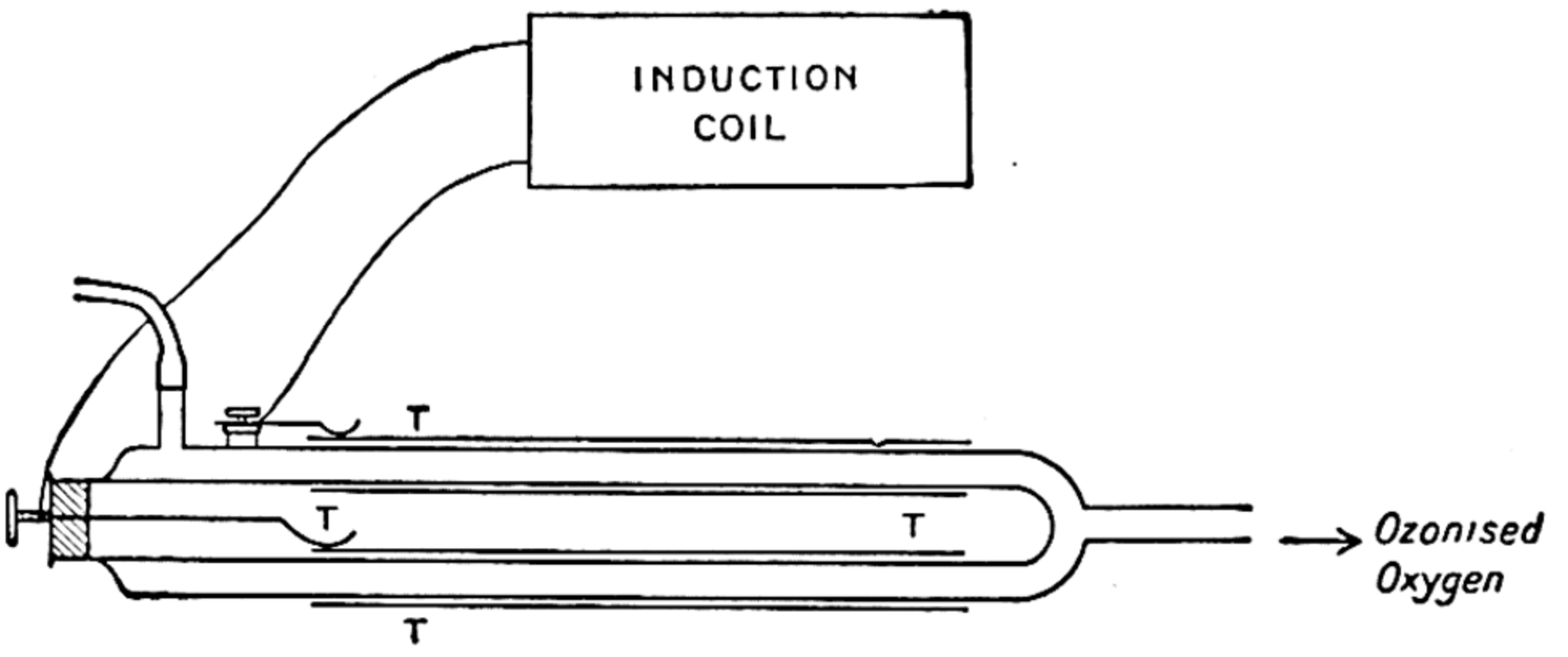



FIG. 158.

be conveniently used for demonstration. The type shown in Fig. 159 is used on the large scale. The discharge takes place between pieces of metal gauze protected by glass plates from the action of the ozone. The electrical discharge method is always employed on the commercial scale.

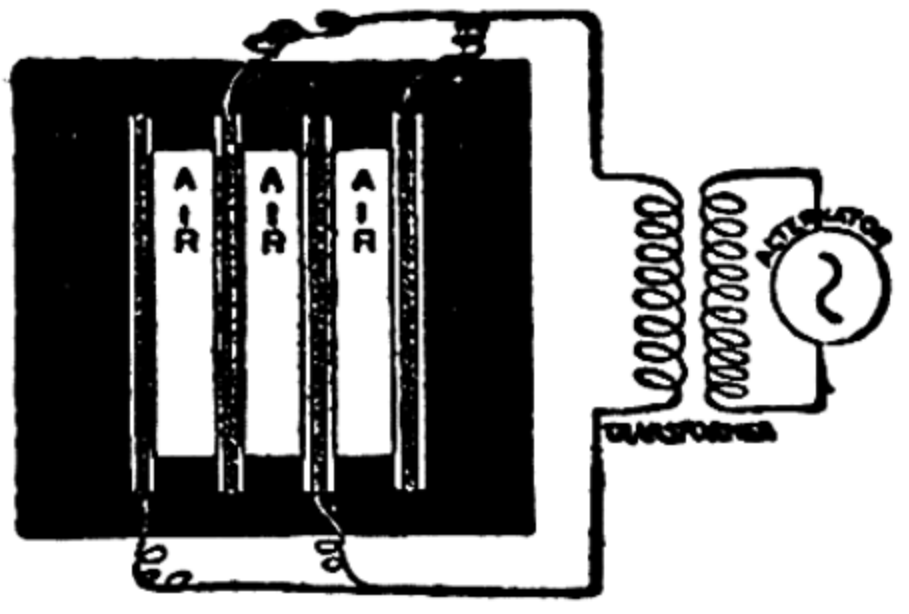



FIG. 159.—Ozoniser. Industrial type.

Ozone may be prepared by various chemical methods, which involve the liberation of oxygen together with much energy. The best of these is the electrolysis of ice-cold dilute sulphuric acid, using an anode of platinum foil so embedded in glass that only the edge is exposed. In this way a very high concentration of energy occurs at the anode and some 20 per cent. of ozone occurs in the gas liberated. When fluorine decomposes water the oxygen produced contains up to 14·4 per cent. of ozone. The reaction of cæsium tetroxide and carbon dioxide liberates much ozone.

Pure ozone has been obtained by cooling ozonised oxygen with liquid air, when ozone, which boils at — 112·4° C., condenses as a very dark blue, highly explosive liquid. By allowing this to evaporate pure ozone is obtained, which, however, soon begins to decompose.

**876. Formula of Ozone.**—Since pure ozone could not for many years be prepared, and in any event cannot be preserved for any appreciable time, peculiar difficulties were found in determining its formula.

Ozonised oxygen on heating yielded nothing but oxygen, and the formula of ozone was thereby shown to be $O_x$.

The problem has been solved by making use of the fact that turpentine absorbs ozone completely. Air is enclosed in the space between the inner and outer tubes of the apparatus shown. The inner tube is filled with a conducting liquid (*e.g.*, dilute sulphuric

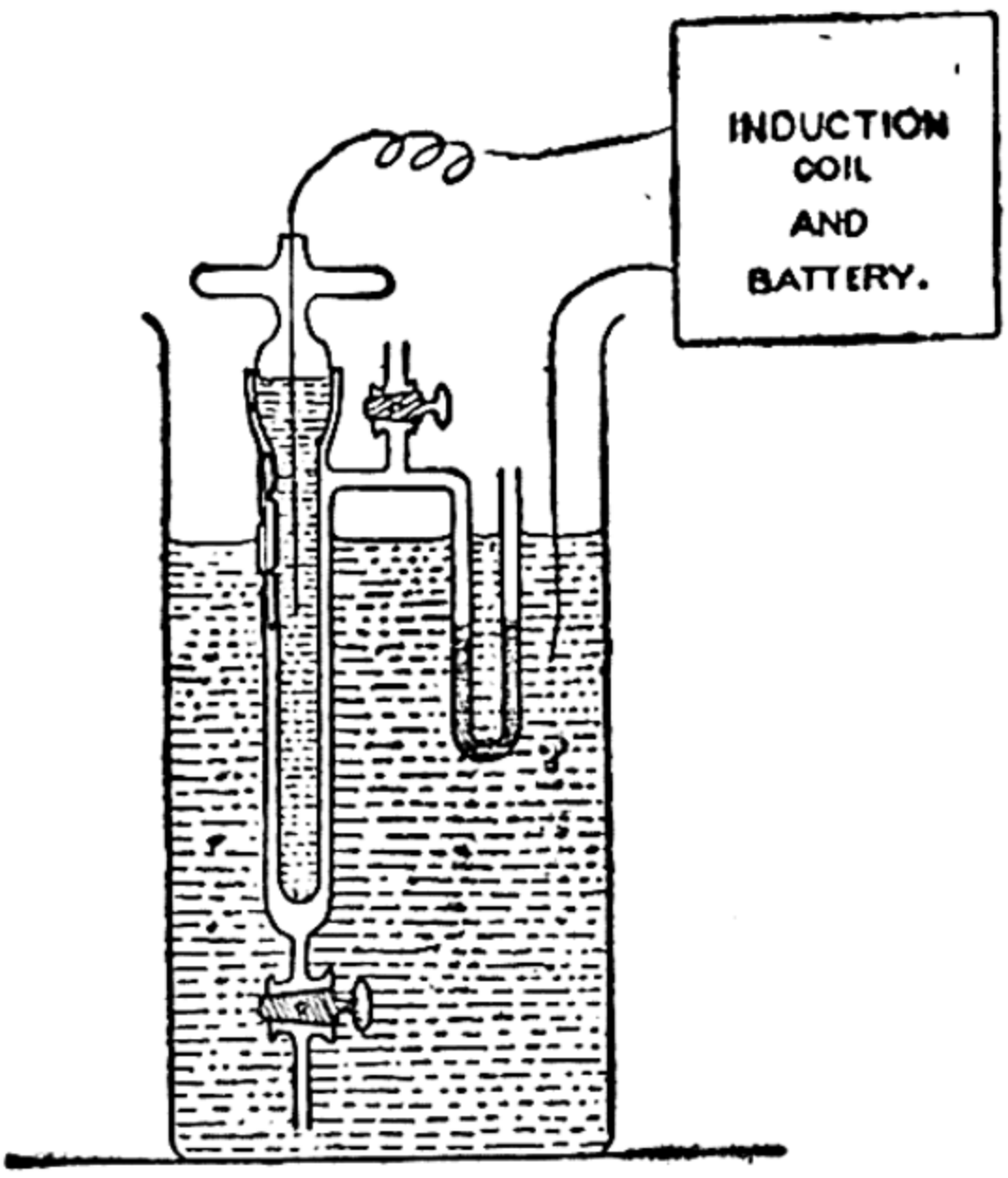



FIG. 160.—Composition of ozone.

acid). A small sealed tube containing turpentine is gripped between projections on the inner tube and on the outer tube. The whole apparatus is then stood in a vessel containing dilute sulphuric acid. Into this vessel and into the inner tube dip wires connected to an induction coil. The silent discharge passes through the air and ozonises a part of it. A contraction takes place and the sulphuric acid in the U-tube rises, say, by $n$ cm. The tube of turpentine is now broken and a further rise of $m$ cm. occurs, due to the absorption of the ozone. Thus a contraction of $n$ volumes occurs when a certain amount of ozone is *formed* and the volume of the ozone formed is $m$ cm. Now it is found that $m$ is always *twice* $n$. Ozone is formed from pure oxygen alone and its formula must be $O_x$. Then, when it is formed we have the equation,

$$2O_x = xO_2,$$

and 2 volumes of ozone are formed from $x$ volumes of oxygen. From the same equation it follows that the contraction in volume when 2 volumes of ozone are formed is $x - 2$ volumes, and so in the above experiment,

$$\frac{n}{m} = \frac{x - 2.}{2}$$

The results of the experiment prove that $\frac{n}{m} = \frac{1}{2}$, so it follows that $x = 3$, and the formula of ozone is therefore $O_3$.

**877. Physical Properties.**—Ozone is a gas perceptibly blue in high concentrations. Liquid ozone is very dark blue in colour. Ozone has a remarkable smell, not unlike chlorine, and is poisonous in concentrations, exceeding some 20 parts per million. It has a powerful oxidising action upon the organic substances which cause the 'stuffy' smell in badly ventilated places, and it is used in the ventilation of the Central London Tube railway.

Liquid ozone is strongly magnetic. It is only partly miscible with liquid oxygen.

Ozone is soluble in water, but the solution is very unstable.

**878. Chemical Properties.**—Ozone very readily decomposes, forming oxygen,

$$2O_3 = 3O_2 + 69 \text{ Cal.}$$

It decomposes almost instantaneously at high temperatures and slowly at room temperatures.

Ozone is one of the most powerful of oxidising agents. Its usual reaction is

$$O_3 + X = O_2 + XO,$$

one atom of oxygen combining chemically and one molecule being liberated.

All metals, except gold and platinum, are oxidised. Hydrogen sulphide is oxidised to sulphuric acid,

$$H_2S + 4O_3 = H_2SO_4 + 4O_2.$$

Potassium iodide is oxidised to iodine,

$$2KI + H_2O + O_3 = 2KOH + O_2 + I_2.$$

Lead sulphide is oxidised to the sulphate,

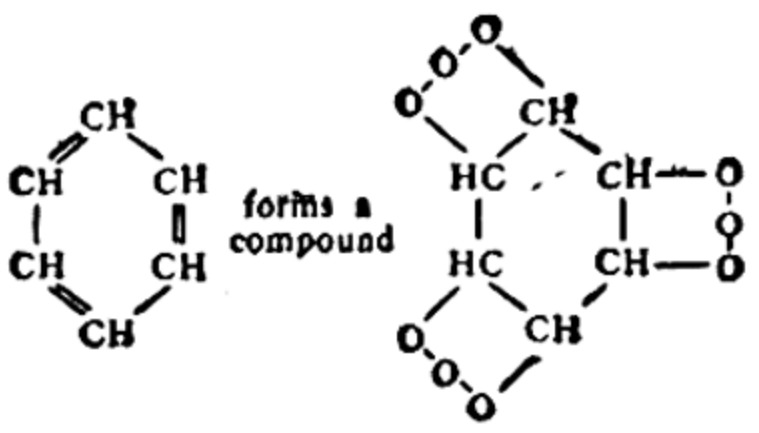
$$PbS + 4O_3 = PbSO_4 + 4O_2.$$

Nitrogen tetroxide is oxidised to the pentoxide,

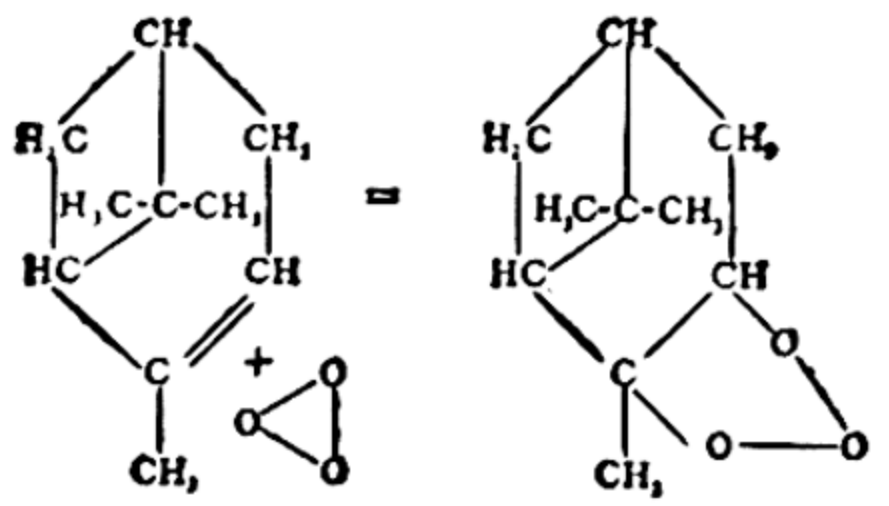
$$O_3 + N_2O_4 = N_2O_5 + O_2.$$

Many organic substances are oxidised. India-rubber is at once attacked, as is also cellulose.

Unsaturated organic compounds do not decompose ozone but absorb it completely, forming ozonides. Thus benzene,




These ozonides are for the most part explosive substances. The main constituent of turpentine, pinene, contains a double bond and forms an ozonide.



Pinene + ozone. Pinene ozonide.

Turpentine, therefore, absorbs ozone completely, and this property is made use of in the determination of the quantity of the gas present in a specimen of ozonised air.

**879. Detection of Ozone.**—Ozone may be detected by its action on mercury. Ozone oxidises mercury, and a trace of ozone causes mercury to stick to glass and to become dull in appearance.

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Most of its reactions, such as that with potassium iodide, are given by other oxidising agents. If a gas is found to liberate iodine from potassium iodide in the cold, but will not do so after passing through a heated tube, ozone or hydrogen peroxide vapour is the oxidising agent present. To distinguish between these the gas may be passed through very dilute permanganate solution, which decomposes and is decolorised by hydrogen peroxide ($_1$ 214), but not ozone.

Ozone is estimated by passing it into potassium iodide solution and titrating the iodine liberated.

**880. Commercial Applications.**—By far the most important use of ozone is in the purification of drinking-water. The water is passed down towers up which ozonised air is flowing and is almost completely sterilised. The process is more popular on the continent and in America than in this country. Ozone is also used for ventilation (§ 877), and as a powerful bleaching agent for wax and certain other materials.

# CHAPTER XX

## SULPHUR

**881. Historical.**—The element sulphur has been known from very early times. It was known to the Egyptians; it is mentioned by Homer and has since then been a material in common use.

The Greeks and Romans used sulphur for fumigation, and the fumes of burning sulphur were used to whiten clothes. In the Middle Ages it was used medicinally, and the invention of gunpowder again increased the demand for it. The sulphuric acid industry to-day uses vast quantities of sulphur, and the quantity used annually exceeds 2,000,000 tons, of which the United States produces some 1,800,000.

**882. Occurrence.**—Sulphur is found in the free state in various parts of the world. It is usually found in volcanic districts, and the

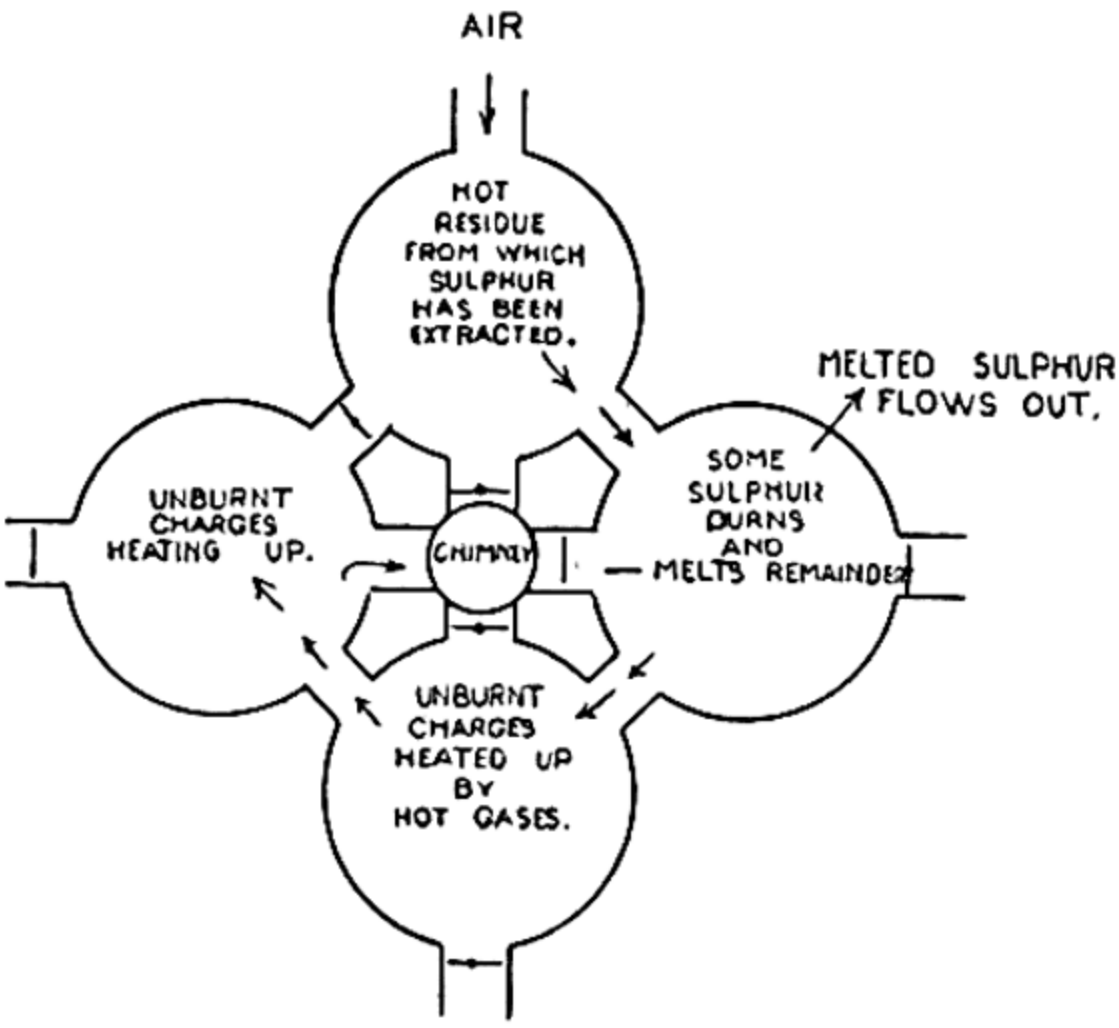



FIG. 161.—Gill's regenerative furnace for extraction of sulphur from its ores.

sulphur mined in Italy and Japan is of volcanic origin. The greatest source of sulphur is, however, the peculiar deposits of sulphur which are found in Louisiana and Texas. These are further described below.

Sulphur occurs combined in the form of sulphides; iron pyrites, copper pyrites, zinc blende, etc., being common minerals containing a high percentage of sulphur.

Sulphates, too, are common minerals; gypsum, calcium sulphate, may be mentioned as an example of these.

**883. Manufacture of Sulphur.**—*Sicilian Sulphur.*—Sulphur occurs in Sicily in a peculiar formation, consisting of gypsum, clay and sulphur, the latter amounting to some 24 per cent. The sulphur is believed to result from the reduction of the gypsum by organic matter to calcium sulphide and the subsequent oxidation of the latter. The sulphur is obtained from the rock by heating it. The sulphur melts and flows out of the rock. Since fuel is expensive in Sicily, the cheapest method of heating the rock is to burn a part of it. In order to make the working economical it is endeavoured to burn as little sulphur as possible, and the Gill regenerative furnace is used

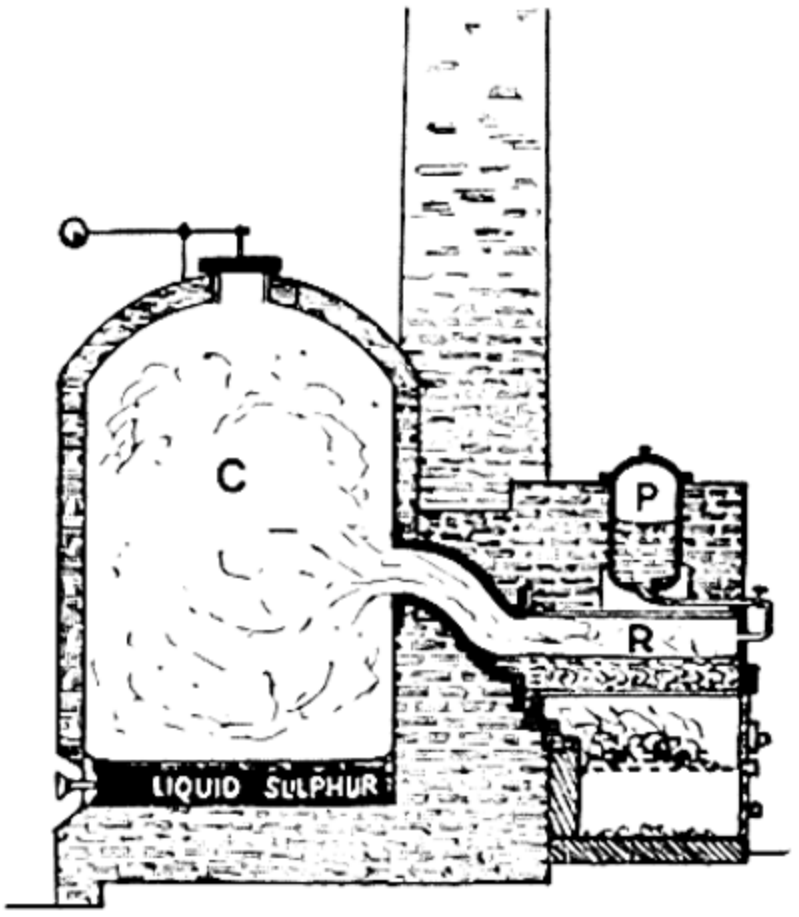



FIG. 162.—Distillation of sulphur.

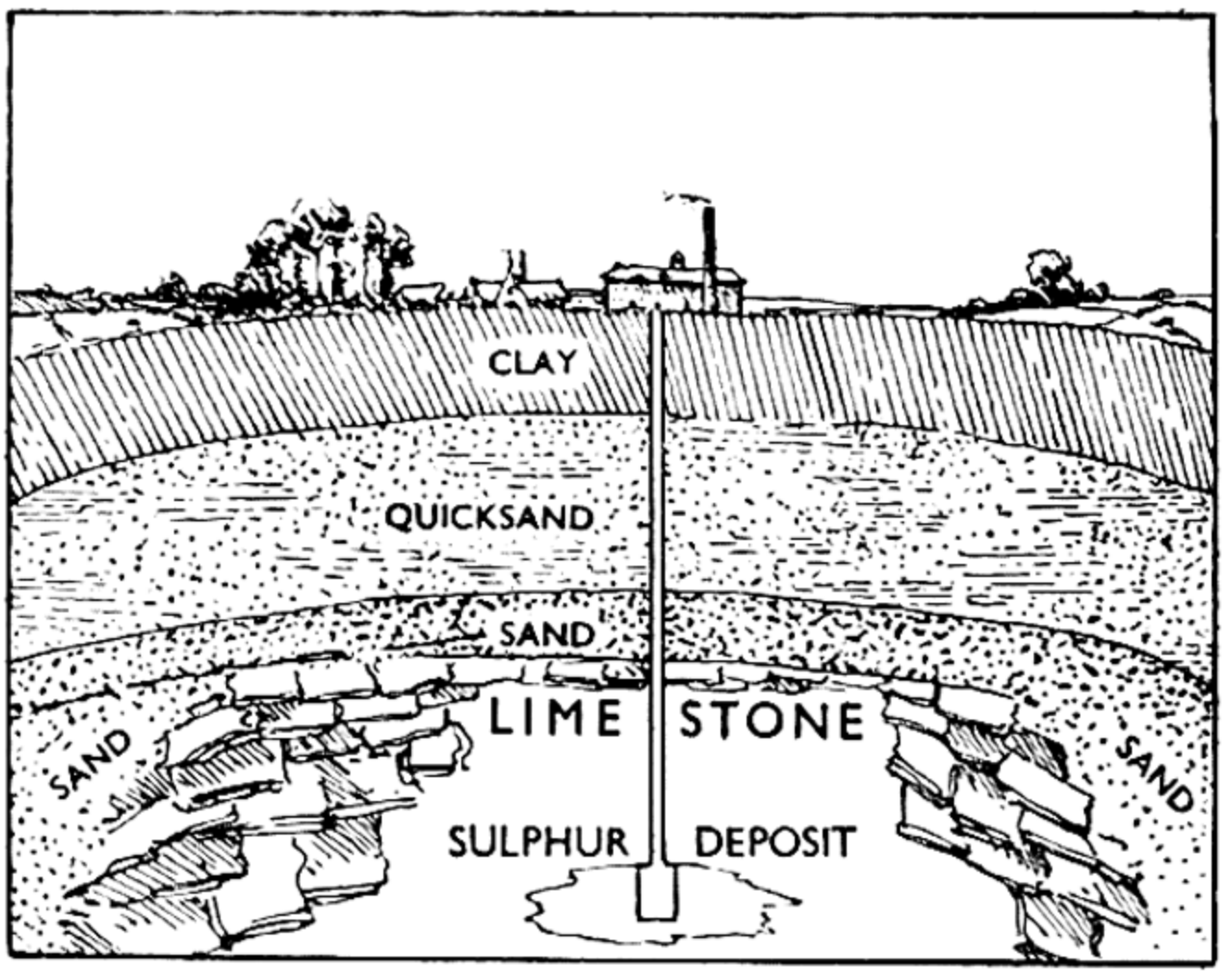



FIG. 162.—American sulphur deposits worked by the Frasch process.

to ensure this (Fig. 161). It consists of a series of chambers with domed roofs. Air enters a chamber in which the sulphur has been melted out of the rock and so takes up some of the heat of the residue of rock. It passes to the next chamber, where some sulphur is burning. This sulphur melts out the remaining sulphur in this kiln. The hot gases then pass through several other kilns and heat up their charges. In this way little heat is wasted. The crude sulphur thus obtained contains from 2 to 10 per cent. of impurity and can be used in this state for many purposes, as for sulphuric acid manufacture,

horticulture, etc., but for certain purposes (gunpowder manufacture, medicine) it has to be refined. This process is performed by distilling the crude sulphur. Fig. 162 shows the type of plant employed for the purpose. R is a retort of fireclay, heated from beneath. P is a reservoir of crude sulphur (kept liquid by the waste heat from the same fire) from which the retort is refilled as the sulphur is used up. The sulphur vapour passes into the brick chamber C. At first it condenses as 'flowers of sulphur,' but as the chamber heats up, it condenses as a liquid, which from time to time is run into moulds.

*American Sulphur.*—The deposits in which sulphur occurs in Louisiana and Texas are peculiar in character. The sulphur bed is overlaid by some 400 feet of clay and quicksands and about 90 feet of limestone. The sulphur bed is on the average 125 feet deep and is very rich in sulphur (about 60 to 70 per cent.). It was found impossible to mine this sulphur by the usual methods, for the presence of great quantities of water rendered the sinking of a shaft difficult; and even when this had been done satisfactorily the poisonous gases, hydrogen sulphide and sulphur dioxide, were found to be present in quantities which would prove fatal to the workmen.

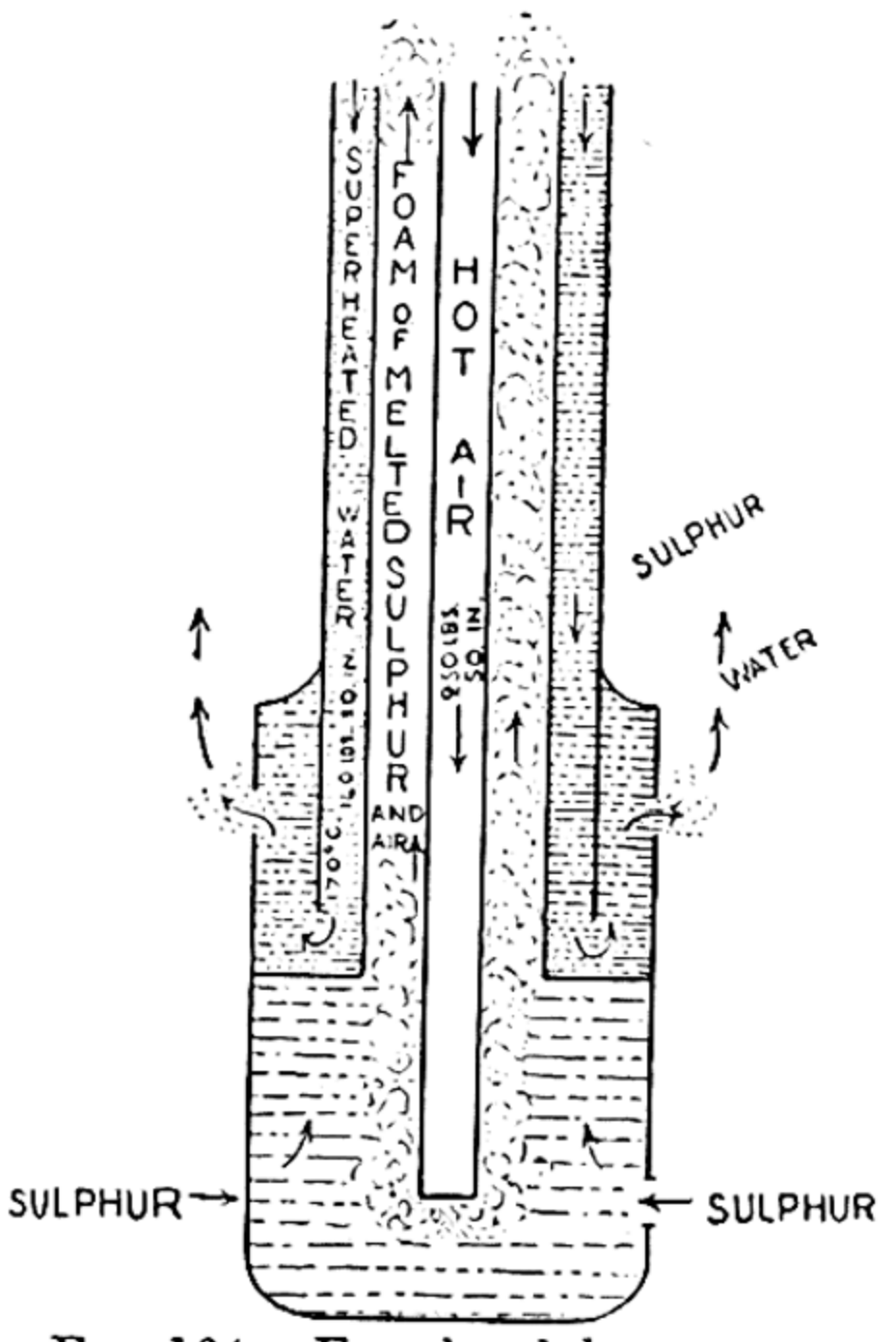



FIG. 164.—Frasch sulphur pump.

Finally, Herman Frasch solved the problem by one of the most ingenious of technical processes.

This process consisted of forcing superheated water under pressure into the sulphur bed, melting the sulphur and forcing it through a tube to the surface. The process employs the apparatus shown in Fig. 164. A boring is sunk into the sulphur deposits and in this is an iron pipe (not shown in the figure). Within this pipe is sunk the Frasch sulphur pump (Fig. 164). Down the outermost of three concentric tubes is forced superheated water at 170–180° C. under a pressure of 140 lbs.[1] (at which pressure it is below its boiling point). This water passes out into the sulphur bed and melts sulphur, which

[1] The pressure at the bottom is much higher, for the hydrostatic pressure of the column of water must be added.

gathers by gravity in a pool round the pump. The sulphur enters the base of the pump, where it meets a stream of air bubbles and is carried to the surface as a foam of air and sulphur. The air bubbles serve to lighten the column of sulphur. The liquid sulphur emerges at the surface and is run into huge bins. A single well may produce 500 tons of sulphur of 99·95 per cent. purity in a single day. The sulphur so produced can be sold at a very low price.

Great quantities of sulphur dioxide, diluted with much air, are produced when sulphide ores (*e.g.*, copper pyrites or zinc blende) are smelted. A process for concentrating this gas and reducing it to sulphur has recently been devised. The diluted gas is scrubbed with a cold solution of sodium sulphite containing an easily hydrolysed salt such as aluminium chloride, so forming sodium bisulphite, $Na_2SO_3 + SO_2 + H_2O \rightleftharpoons 2NaHSO_3$. When the liquor is heated the reverse action takes place, this being aided by the hydrolysis of the aluminium chloride to hydrochloric acid. The pure sulphur dioxide is passed over white-hot coke at 1,100° C., and is thus reduced to sulphur, which is condensed.

$$SO_2 + C = CO_2 + S.$$

A certain amount of sulphur is recovered from alkali waste. The Leblanc process (§ 235) yields calcium sulphide CaS as a waste product. This is now treated by the Chance-Claus process. The principle of the process is the action of carbon dioxide from lime kilns upon the alkali waste mixed to a cream with water.

$$CaS + CO_2 + H_2O = CaCO_3 + H_2S.$$

The hydrogen sulphide produced is passed, mixed with air, over ferric oxide heated to a red heat. This acts catalytically and the reaction

$$2H_2S + O_2 = 2H_2O + 2S$$

takes place. The sulphur vapour formed is passed into chambers where it condenses.

*Purification of Sulphur.*—Sulphur is best obtained in a high state of purity by recrystallisations from carbon disulphide (*v. infra*).

**884. Allotropic Forms of Sulphur.**—Sulphur exhibits a remarkable and complex series of forms. Only two of the solid forms of sulphur can certainly be regarded as true allotropes :—

α-sulphur, octahedral or rhombic sulphur.

β-sulphur, monoclinic sulphur.

In addition to these true allotropes, which have definite and fixed properties, there exist also :—

δ-sulphur, amorphous sulphur, which is probably only very finely divided α-sulphur.

Plastic sulphur, which is probably a gel and therefore a mixture of two forms.

Nacreous sulphur, a crystalline modification, the true nature of which does not appear to be settled.

Colloidal sulphur, milk of sulphur, etc., which are simply amorphous sulphur in a finely-divided condition.

Liquid sulphur contains at least two forms :—

$\lambda$-sulphur.

$\mu$-sulphur.

The existence of a third liquid form $S\pi$ has been postulated.

Sulphur vapour probably contains four allotropes, at least, $S_8$, $S_6$, $S_4$, $S_2$, and these molecules also exist in solution.

**885. Relationships of the Forms of Sulphur.**—Of the forms of solid sulphur only two appear to be permanently stable. $\alpha$-sulphur is stable below 95·5° C. and $\beta$-sulphur above 95·5° C. and below 120° C. The diagram illustrates the conditions of stability of the various forms of sulphur. The ordinates represent the *vapour pressure* of

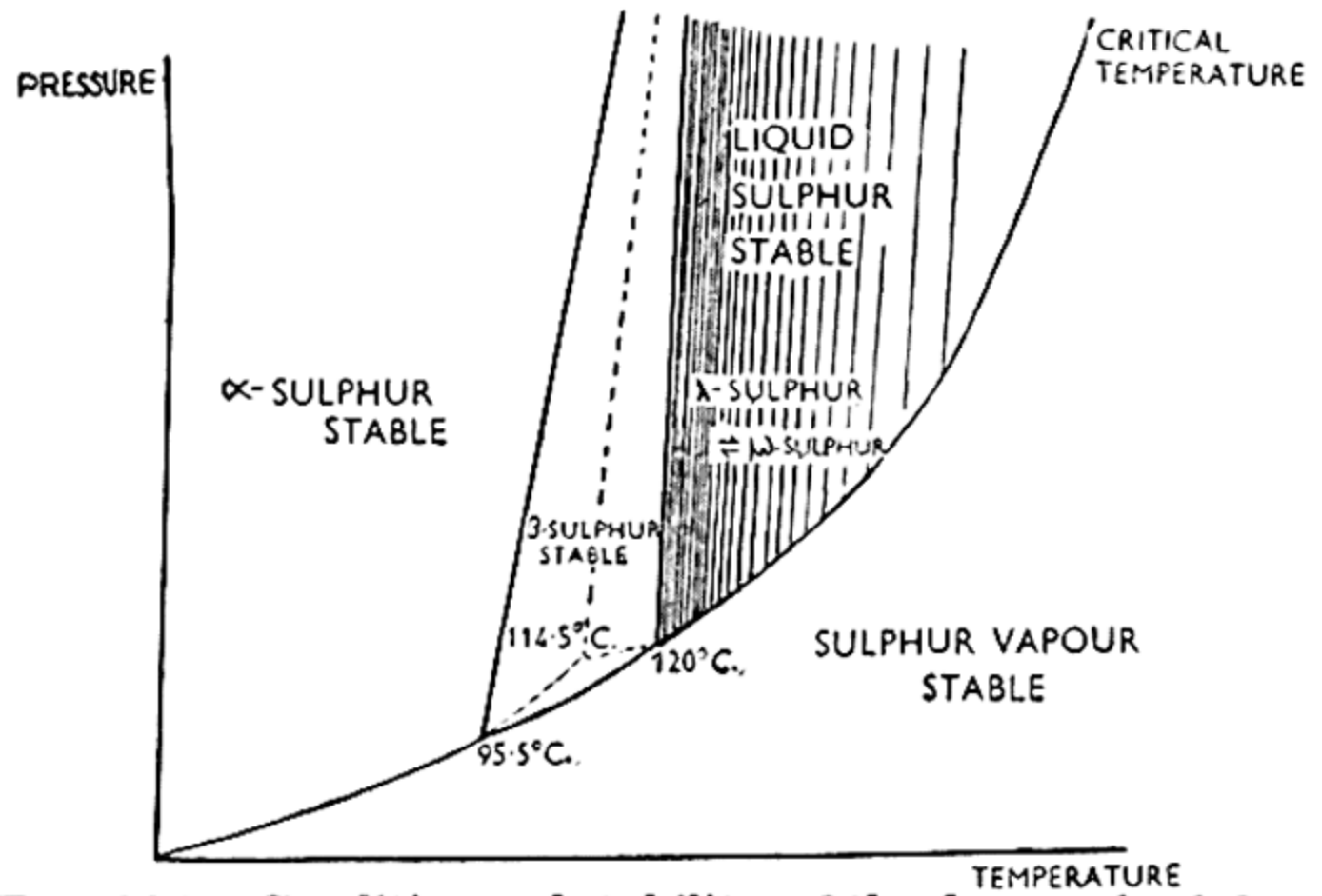



FIG. 165.—Conditions of stability of the forms of sulphur.

sulphur and the abscissæ the temperature. The scale of the vapour pressure is distorted in order to show the relationships more clearly.

The areas in the diagram represent the conditions of temperature and pressure under which each form of sulphur is stable and permanent. Lines represent conditions under which *two* forms can co-exist, and points where three lines meet represent the conditions under which *three* forms can remain permanently in contact without change.

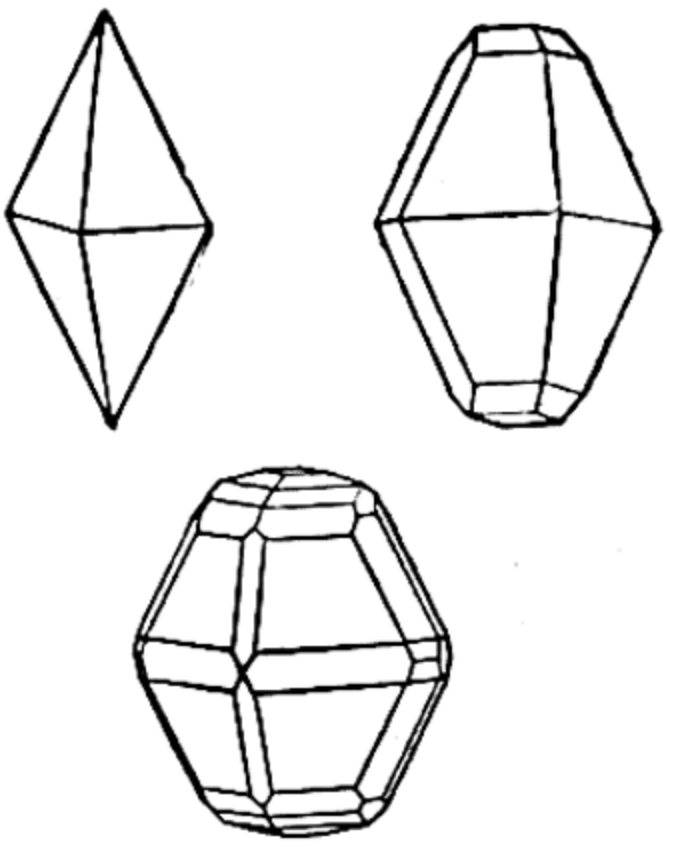
The diagram does not represent the forms which are *never* stable. It also cannot represent "homogeneous equilibria," such as the co-existence of three or four different molecular species of sulphur vapour or two forms of liquid sulphur.

**886. $\alpha$-Sulphur, Rhombic or Octahedral Sulphur.**—It will be seen from Fig. 165 that this form is stable below 95·5° C. at ordinary pressures. We make it, then, by allowing any other form of sulphur to remain for a sufficient time at the ordinary temperature, or by crystallising sulphur below 95·5° C. The latter is the usual course. Sulphur is well ground and shaken in a stoppered bottle with, say, three times its weight of carbon disulphide. The solution is filtered

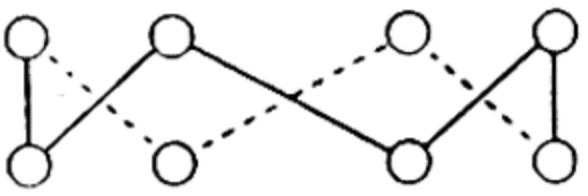
from any residual sulphur and is placed in a crystallising dish covered with a glass plate. As the carbon disulphide evaporates well-formed octahedral crystals appear. Native sulphur is always found as α-sulphur.

*α-sulphur* forms fine transparent amber-coloured crystals. The natural form is an octahedron, but as a rule the edges and corners are bevelled off and the form resembles those delineated in Fig. 166 and Plate XV. When heated to 95·5° C. it becomes opaque and expands, forming monoclinic or β-sulphur. Its density is 2·06. If heated rapidly it melts at 114·5° C., before monoclinic sulphur is formed. Its molecule has been shown to be an eight-membered puckered ring of atoms (Fig. 166).

**887. β-Sulphur, Monoclinic or Prismatic Sulphur,** is stable



Crystals of α-sulphur. From Mellor's *Comprehensive Treatise of Inorganic and Theoretical Chemistry*, by permission of Messrs. Longmans, Green & Co.



Structure of molecule of α-sulphur.

Needle of β-sulphur.

FIG. 166.

between 95·5° C. and 120° C. and is prepared by crystallising sulphur above 95·5° C. The usual method of obtaining it is simply to melt sulphur and allow it to solidify, which takes place at 120° C. if the sulphur is pure, but usually at a rather lower temperature. If crystals are required the sulphur may be melted in a vessel such as a large crucible, and allowed to cool until a thin skin of crystals has covered the surface. This skin is then pierced with a hot iron and the liquid contents of the crucible poured out. It will be found that monoclinic crystals have formed on the walls of the crucible. The form of these is difficult to perceive clearly, but is actually that shown in Fig. 166 and Plate XVB. The structure of the molecule of β-sulphur is more complex than that of α-sulphur and has not been elucidated.

**888. $\gamma$-Sulphur, Plastic Sulphur.**—When molten sulphur at a temperature of above 200° C. is poured into water, plastic sulphur results. This may be done by heating molten sulphur in a crucible till it burns, and then pouring the still burning sulphur in a thin stream into water. If the sulphur used is pure the plastic sulphur is pale yellow, but as made from roll sulphur it is often nearly black. It is a transparent rubber-like elastic mass, and is probably a *gel* like rubber, glue, etc. It hardens within a few days and forms a peculiar variety of sulphur which, like plastic sulphur itself, is insoluble in carbon disulphide.

Plastic sulphur was formerly thought to be super-cooled $\mu$-sulphur, but it is theoretically necessary that the unstable $\mu$-sulphur should be more soluble in carbon disulphide, etc., than the stable forms. Liquid sulphur shows the Tyndall effect (§ 93), and is therefore probably a sol, possibly a suspension of liquid $S_\mu$ in $S_\lambda$. Sols, when they solidify, often give rise to gels. X-ray studies show that its molecule consists of long chains of sulphur atoms.

**889. $\delta$-Sulphur or Amorphous Sulphur.**—When sulphur is precipitated chemically, as by acidifying calcium pentasulphide solution, or by oxidising hydrogen sulphide solution in the cold, amorphous sulphur is precipitated in a form *soluble* in carbon disulphide.

It has recently been claimed that this form is identical with $\alpha$-sulphur and differs only in its state of division.

The sulphur obtained in this way is almost white and is termed milk of sulphur. After some years at the ordinary temperature or more rapidly on heating, it is transformed into ordinary $\alpha$-sulphur.

**890. Colloidal Sulphur** is prepared by the reaction of hydrogen sulphide and sulphurous acid or by the action of sulphuric acid on sodium thiosulphate. It is readily prepared by mixing equivalent solutions of hydrogen sulphide and sulphur dioxide.

It forms a clear yellow solution containing very minute suspended particles of sulphur. The addition of a little alum at once precipitates the sulphur.

**891. Nacreous sulphur** forms plates with a mother-of-pearl-like lustre, and is obtained by crystallising sulphur from its solutions in benzene, etc., under special conditions. Nacreous sulphur is monoclinic, but the angles of its crystals are not the same as of $\beta$-sulphur. Several other less common crystalline varieties have been claimed.

**892. Forms of Liquid Sulphur.**—When sulphur is melted the liquid formed at 120°–130° C. is of a clear amber tint and is as mobile as water. On warming this to 160° C. it sharply becomes exceedingly viscous, so much so that it cannot be poured from an inverted vessel. This viscous liquid becomes less viscous when still further heated, and at the same time becomes very deep red-brown

in colour. These peculiar changes are due to the existence of two liquid forms of sulphur ($S_\lambda$, lambda-sulphur, and $S_\mu$, mu-sulphur) in dynamic equilibrium,

$$S_\lambda \rightleftharpoons S_\mu.$$

These forms do not appear to be fully miscible, but form a sol (§ 888). The amber-coloured mobile liquid is pure $S_\lambda$, and it solidifies to monoclinic sulphur when cooled. As the temperature rises increasing quantities of $S_\mu$ are formed, and at the boiling point of sulphur the liquid consists mainly of $S_\mu$. $\mu$-sulphur, when rapidly cooled, forms plastic $\gamma$-sulphur, but when slowly cooled it reverts to $\lambda$-sulphur, which then solidifies to the monoclinic form.

**893. General Properties of Sulphur.**—Sulphur is a yellow or white solid without taste or smell. It has little or no physiological effect on man, but its vapour is very poisonous to certain low forms of life, such as fungi, mites, etc. Sulphur is brittle, and a poor conductor of heat. It is a non-conductor of electricity and has been used as an insulator ; its brittleness and its effect on metals prevent its general use. Sulphur has a density 1·96 to 2·06 ($S_\alpha$ 2·06, $S_\delta$ 2·04, $S_\beta$ 1·96). It melts, if heated slowly enough, at the melting point of $\beta$-sulphur, 120° C., but under normal conditions at about 115° C. Sulphur boils at 444·5° C., and its boiling point forms a useful fixed point in thermometry.

Sulphur is insoluble in water, sparingly soluble in alcohol, ether, chloroform, etc., but very soluble in carbon disulphide (1 : 2·5 in cold, 1 : 1·821 at 55° C.). It is moderately soluble in benzene.

**894. Chemical Properties.**—Sulphur burns in air with a blue flame, forming sulphur dioxide and a little sulphur trioxide.

$$S_\alpha + O_2 = SO_2 + 71{,}080 \text{ cals.}$$

$$2SO_2 + O_2 \rightleftharpoons 2SO_3.$$

Its temperature of ignition is low, *c.* 250° C., which makes it a useful combustible in match heads. The monoclinic variety evolves 71,720 cals. in comparison with the rhombic 71,080. In oxygen sulphur burns with a beautiful violet flame.

Mixed with substances which readily give up oxygen, sulphur deflagrates or explodes. Gunpowder (sulphur 1 part, carbon 1 part, potassium nitrate 6 parts) is an example of this action.

Sulphur reacts with carbon to form carbon disulphide (*q.v.*). With phosphorus, arsenic and the majority of the metals, sulphides are formed on heating the elements together.

$$2P + 5S = P_2S_5$$
$$2As + 3S = As_2S_3$$
$$Hg + S = HgS, \text{ etc.}$$

The halogens react with sulphur, forming various halides, $SF_6$, $S_2Cl_2$, etc. (*q.v.*).

Sulphur is unattacked by water and by such acids as are not also oxidising agents. Concentrated sulphuric acid and nitric acid oxidise it to sulphur dioxide and sulphuric acid respectively,

$$S + 2H_2SO_4 = 2H_2O + 3SO_2$$
$$S + 6HNO_3 = H_2SO_4 + 2H_2O + 6NO_2.$$

Both reactions are slow. The latter is much accelerated by the addition of bromine (see p. 126).

Sulphur reacts with alkalis, forming sulphides and thiosulphates. Thus with caustic potash, potassium thiosulphate and sulphide first result,

$$6KOH + 4S = K_2S_2O_3 + 2K_2S + 3H_2O.$$

The potassium sulphide combines with more sulphur, forming the pentasulphide which has

$$K_2S + 4S = K_2S_5,$$

a red-brown colour. Solutions containing calcium thiosulphate and pentasulphide obtained by the action of lime on sulphur have been known since the first century of the Christian era and have found various industrial uses (§ 374).

*Uses of Sulphur.*—Sulphur finds its chief uses :—

(1) In the manufacture of calcium and magnesium bisulphite for bleaching wood pulp. Some 200,000 tons are used yearly for this purpose (§ 375).

(2) For dusting vines and hops, which suffer from a form of *oidium* or mould fungus. Some 100,000 tons are used yearly in this way.

(3) In the manufacture of sulphuric acid (§§ 929 *seq.*), which is itself used in the manufacture of a great variety of products. Pyrites is a cheaper source of sulphur, but the element has the advantage of being arsenic-free.

(4) Large quantities are employed in the vulcanisation of rubber and for making sulphur chloride—used in this industry.

(5) Sulphur finds uses in the manufacture of explosives, fireworks and matches.

(6) Sulphur is used for making carbon disulphide, sulphur dioxide, etc. It is also used in medicine made up as an ointment, etc.

(7) Sulphur is also used in the manufacture of the sulphide dyes, which are both cheap and very fast.

**895. Atomic Weight of Sulphur.**—That the atomic weight of sulphur is very nearly 32, appears from the vapour densities of its many volatile compounds. These never contain less than 32 gms. of sulphur per gram-molecule.

Library
Srinagar

Exact values for the atomic weight of sulphur have been obtained in many ways. The best determinations are probably those of Richards and his collaborators. They converted sodium carbonate into sodium sulphate and so obtained the ratios of their weights. They also converted silver sulphate into the chloride by heating it in a stream of hydrogen chloride. These methods gave results of 32·06. The determination of the densities of sulphur dioxide and hydrogen sulphide give values of 32·05 to 32·07. The value $32{\cdot}06_5$ is generally adopted.

**896. Valency of Sulphur.**—Sulphur readily forms compounds with both non-metals and metals. The compounds with non-metals are non-polar and those with metals for the most part polar, *i.e.*, salts. The sulphur atom has the electronic structure, 2, 8, 6. It can combine to form a polar compound by taking up two electrons, forming the ion $S^{--}$ with the electronic structure, 2, 8, 8. In its covalent compounds it has six electrons to share, and accordingly its maximum valency should be six. This is exhibited in the compound $SF_6$,

in which sulphur has a ring of twelve electrons surrounding it. This is uncommon, and normally a ring of eight is all that is found.

**897. Hydrogen Sulphide. Sulphuretted Hydrogen $H_2S$.**—The odour of hydrogen sulphide must have been associated with putrefaction from the earliest times. The first scientific examination of the gas was, however, made by Scheele in 1777.

Hydrogen sulphide is found in volcanic gases and impregnates the water of many mineral springs, such as those of Harrogate, Llandrindod Wells, Aix-la-Chapelle, etc. These springs are believed to have a medicinal value, acting especially upon the liver. As a product of the putrefaction of sulphur-containing organic matter it is found in sewer-gas and also in highly polluted rivers. The lower depths of the Black Sea contain a notable proportion of the gas.

**898. Preparation of Hydrogen Sulphide.**—The gas hydrogen sulphide may be prepared :—

(*a*) By the action of hydrogen upon sulphur or certain sulphides.
(*b*) By the action of acids or water upon sulphides.
(*c*) By the action of sulphur upon organic matter.

(*a*) If a stream of hydrogen be passed through boiling sulphur a little of the gas is formed ; the method is not of practical value,

$$S + H_2 \rightleftharpoons H_2S.$$

When hydrogen is passed over certain sulphides they are reduced with formation of hydrogen sulphide,

$$Sb_2S_3 + 3H_2 = 2Sb + 3H_2S.$$

(*b*) The action of dilute sulphuric or hydrochloric acid upon ferrous sulphide is by far the most convenient means of preparing the gas. The gas thus prepared contains acid and iron salt mechanically carried over as spray, and also hydrogen derived from the metallic iron always present as impurity in the sulphide. The first two impurities are readily removed by washing the gas with a little water.

Various types of apparatus are in use to ensure a supply of the gas, which is continually required in a laboratory where qualitative analysis is performed. There are numerous patterns, but that illustrated is simple and easy to handle. It works on the same principle as Kipp's apparatus; but, since it holds a much greater quantity of material, it needs re-filling less often.

A purer gas is obtained by the action of hydrochloric acid (2 parts conc. : 1 part water) upon antimony sulphide, preferably the artificially prepared material. The gas should be washed with water.

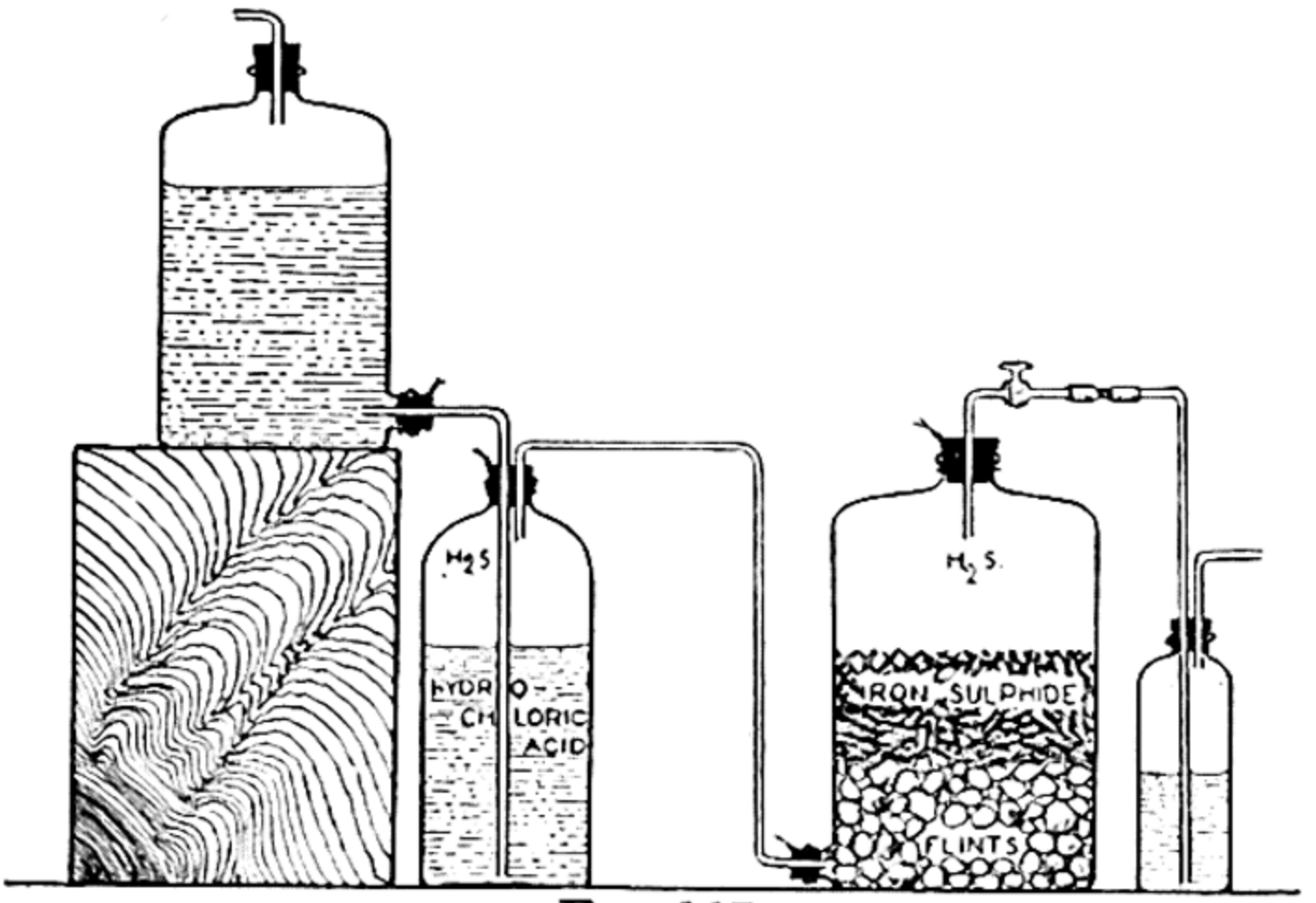



FIG. 167.

$$Sb_2S_3 + 6HCl \rightleftharpoons 2SbCl_3 + 3H_2S.$$

Aluminium sulphide is decomposed by water, yielding the gas,

$$Al_2S_3 + 6H_2O \rightleftharpoons 2Al(OH)_3 + 3H_2S.$$

(*c*) Sulphur, when heated with vaseline, paraffin wax, and many other hydrogen-containing organic compounds, yields hydrogen sulphide.

Very pure hydrogen sulphide is best obtained by solidifying the gas with liquid air and removing all uncondensed gas (hydrogen) with a pump. On allowing the solid to warm up, impurities boil off first, and after a part has boiled away the gas evolved is pure hydrogen sulphide.

Hydrogen sulphide may be collected over hot water, but it is rather too soluble to collect in cold water. If it is required dry

calcium chloride should be used as drying agent. Alkalis absorb it and sulphuric acid slowly oxidises it,

$$H_2SO_4 + 3H_2S = 4H_2O + 4S.$$

**899. Formula.**—If hydrogen sulphide be heated with tin—the apparatus of Fig. 168 is suitable—hydrogen is produced and the volume of the latter is equal to that of the hydrogen sulphide. Thus 1 volume hydrogen sulphide contains 1 volume hydrogen and by Avogadro's hypothesis, 1 molecule of hydrogen sulphide contains 1 molecule of hydrogen. Its formula is, therefore, $H_2S_n$. Since its density is 17, its molecular weight is 34 and the weight of sulphur in the molecule is $34 - 2 = 32 = 1$ atomic weight. The formula is therefore $H_2S$.

**900. Physical Properties.**—Hydrogen sulphide is a colourless gas with a very unpleasant odour recalling that of a rotten egg. The smell of the purified gas is less disagreeable. It has a sickly taste, recalling its smell.

The gas is highly poisonous, an atmosphere containing 1 part in 1,000 being rapidly fatal. Its smell, however, prevents any danger of poisoning in the laboratory, for an atmosphere of 1 part in 100,000 of air is unpleasantly fetid. Cases of poisoning arise chiefly in sewers, etc.; very dilute chlorine is the best remedy, but must be applied with care lest the remedy be worse than the disease.

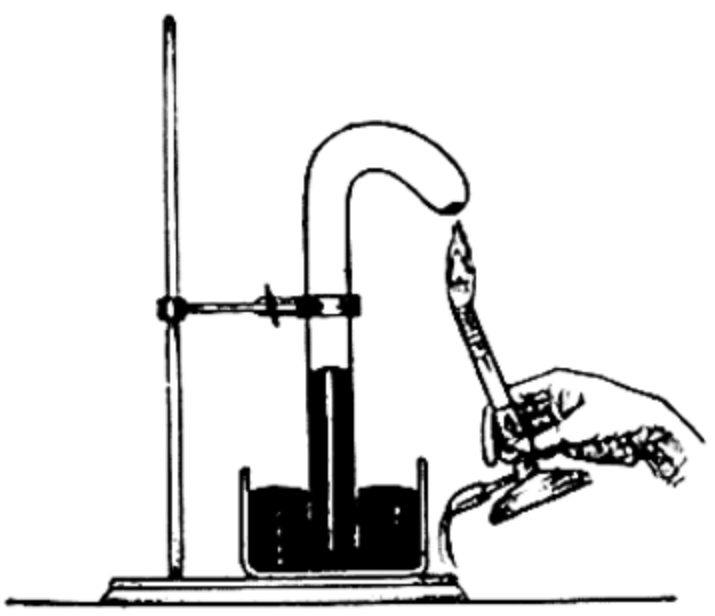


FIG. 168.—Composition of hydrogen sulphide.

The gas is a little heavier than air ($D = 17$, $H_2 = 1$). It is readily liquefied and boils at $-61°$ C. and freezes at $-82{\cdot}9°$ C. Water dissolves 4·4 times its volume of the gas at 0° C. and 3·2 volumes at 15° C. The solution forms a useful reagent.

The physical and, to a less extent, chemical properties of hydrogen sulphide $H_2S$ are in decided contrast to that of its analogue, water, $H_2O$. The latter is an associated substance; accordingly it has a much higher boiling point and melting point than hydrogen sulphide. The tendency of hydrogen sulphide to form co-ordinate compounds is negligible, whereas water acts both as a donor and acceptor, forming a great variety of such compounds. The reason for this difference is not apparent.

**901. Chemical Properties.**—Hydrogen sulphide readily burns in air with a blue flame. If excess of air is present sulphur dioxide and water are the products; with a deficit of air sulphur is produced and

the flame consequently deposits sulphur on any cold object placed in it.

$$2H_2S + O_2 = 2H_2O + 2S$$
$$2H_2S + 3O_2 = 2H_2O + 2SO_2.$$

The former reaction is utilised in the Chance-Claus process (*v.* p. 620). Its solution in water oxidises at the ordinary temperature in accordance with the first of the above equations.

Hydrogen sulphide reacts with the halogens, forming the hydrogen halides and sulphur,

$$H_2S + Br_2 = 2HBr + S.$$

If excess of halogen is present the sulphur will be affected. The reaction is utilised for making hydrogen bromide and iodide (§§ 1078, 1094).

Hydrogen sulphide is a reducing agent. It reduces ferric salts to ferrous salts,

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$$
$$K_2Cr_2O_7 + 5H_2SO_4 + 3H_2S = 2KHSO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S,$$

dichromates to chromium salts, etc., sulphur being deposited. Among such reactions may be noted its reaction with sulphur dioxide,

$$SO_2 + 2H_2S = 2H_2O + 3S,$$

which takes place only in presence of liquid water. The experiment may be performed by mixing the gases, not specially freed from water-vapour, by superposing a gas-jar of sulphur dioxide upon one of hydrogen sulphide. If the jars are dry no reaction takes place. On introducing liquid water sulphur is at once deposited.

The reaction is actually more complex than the above equation would indicate, for in addition to sulphur, polythionic acids (§ 940) are produced.

Hydrogen sulphide is occasionally used as a reducing agent in organic chemistry.

The reaction of hydrogen sulphide with heated metals yields, as a rule, hydrogen and a sulphide. In this respect it behaves as an acid,

$$Sn + H_2S = SnS + H_2.$$

In solution hydrogen sulphide has the reactions of a weak acid and its solution is sometimes called hydrosulphuric acid. The solution is a better conductor of electricity than pure water, showing that ionisation takes place,

$$H_2S \rightleftharpoons H^+ + HS^- \rightleftharpoons 2H^+ + S^{--}.$$

With the alkalis it forms salts called hydrosulphides and sulphides

$$H_2S + KOH = KHS + H_2O$$
$$H_2S + 2KOH = K_2S + 2H_2O.$$

**902. Reaction of Hydrogen Sulphide with Solutions of Metallic Salts.**—Most of the sulphides of the metals are insoluble in water, those of the alkali metals being exceptions. The sulphides of the alkaline earth metals, aluminium, chromium and the rare-earths, are decomposed by water. The sulphides of the remaining metals are to be divided into two classes.

(1) Those insoluble in acids (say 2N hydrochloric).

(2) Those dissolved by acids.

The first class includes the sulphides of gold, silver, mercury, copper, lead, bismuth, arsenic, antimony, tin and cadmium; the second, those of iron, nickel, cobalt, zinc, and manganese. Thus, if hydrogen sulphide is passed through an acid solution of a salt of the first class of metals the sulphide is precipitated. From a solution of a salt of a metal of the second class the sulphide is only precipitated if acid is not present. Since the reaction of, say, a chloride with hydrogen sulphide *produces* an acid, the reaction will only be complete if

$$FeCl_2 + H_2S \rightleftharpoons FeS + 2HCl,$$

an alkali is present to remove the acid as fast as it is formed.

The full explanation of the matter is given by the theory of electrolytic dissociation.

No sulphide is altogether insoluble, for even the most "insoluble" substances dissolve to some extent. The small amount of any sulphide present in solution will ionise. Thus, if any solid sulphide (MS) is precipitated,

$$\underset{\text{Solid.}}{MS} \rightleftharpoons M^{++} + S^{--}.$$

As shown in § 118, the sulphide is precipitated when

$$[M^{++}]\,[S^{--}] > S,$$

where $S$ is the *solubility product* of the particular sulphide.

The condition then that the solution shall be saturated with the sulphide is that the product of the concentrations of the metallic ion $M^{++}$ and the sulphide ion $S^{--}$ shall reach a certain value $S$, depending on the nature of the sulphide in question. If this value $S$ is *exceeded* the solid sulphide will be precipitated. Let us suppose that we are to saturate with hydrogen sulphide solutions of various metallic salts of equivalent strength so that $[M^{++}] = 1$ gm.-mol. per litre or any other arbitrary value in each case.

Then in order that precipitation shall take place,

$$1 \times [S^{--}] = S.$$

Now, in a neutral solution of hydrogen sulphide, which is a very weak acid,

$$H_2S \rightleftharpoons 2H^+ + S^{--},$$

and

$$\frac{[H^+]^2\,[S^{--}]}{[H_2S]} = k',$$

and since, if the solution is saturated with hydrogen sulphide. $[H_2S]$ is constant,

$$[H^+]^2\,[S^{--}] = k'[H_2S] = k''$$

and

$$[S^{--}] = \frac{k''}{[H^+]^2}.$$

The concentration of sulphide ion, then, varies inversely as the square of the concentration of hydrion present.

The addition of acid to a solution of hydrogen sulphide will then increase $[H^+]$ and, by so doing, diminish the concentration of sulphide ion, until in some cases, it may fall to a value where $[M^{++}][S^{--}] < S$ and so prevent the precipitation of the sulphide. Some sulphides have so small a solubility product that the maximum possible concentration of hydrion (about 5N) will not diminish the concentration of sulphide ion enough to prevent their precipitation. This is the case with some of the metals of Group II. A in the qualitative analysis tables: but antimony and cadmium occupy an intermediate position, being precipitated if the concentration of hydrion is less than about 3N. The remaining metals, iron, zinc, cobalt, nickel and manganese, need a fairly large concentration of sulphide ion and therefore a very small concentration of hydrion to cause their precipitation. This condition is attained by adding hydroxyl ion in the form of alkali and neutralising the acid present by removing the $H^+$; for, since in water $[H^+][OH^-] = 10^{-14}$, the addition of $OH^-$ causes a great diminution in the concentration of hydrion and consequent increase of the concentration of sulphide ion.

**903. Uses of Hydrogen Sulphide.**—In addition to its use in analysis, it is used on the large scale for removing arsenic from sulphuric acid by precipitating it as arsenic trisulphide.

**904. Detection and Estimation.**—Hydrogen sulphide is readily detected by its action upon metallic salts. Paper soaked in a solution of lead acetate (or better, sodium plumbite) turns first brown and then black when in contact with the gas,

$$Pb\bar{A}_2 + H_2S = PbS + 2H\bar{A}.$$

The gas is estimated by titration with iodine, the reaction being

$$H_2S + I_2 = 2HI + S.$$

**905. The Sulphides.**—The sulphides of the non-metals are usually prepared by the direct interaction of sulphur and the non-metal in question (exception, nitrogen sulphide, § 756).

The metallic sulphides are prepared :—

(1) By heating the metal with sulphur.
(2) By heating certain compounds of the metal with sulphur
(3) By the reduction of the sulphates of the metals with carbon.
(4) By precipitation with hydrogen sulphide, as described in § 902.
(5) By the action of hydrogen sulphide upon alkalis.

Sodium and potassium sulphides are the only soluble sulphides (other than polysulphides). They are made by method (5).

Their solutions are strongly alkaline as a result of hydrolysis,

$$K_2S + 2H_2O \rightleftharpoons 2KOH + H_2S,$$

and smell of hydrogen sulphide.

The sulphides of the alkaline earths are insoluble in water but are more or less readily decomposed by it,

$$CaS + 2H_2O \rightleftharpoons Ca(OH)_2 + H_2S.$$

The sulphides of aluminium and chromium and the rare-earths are decomposed by water,

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S.$$

The insoluble sulphides as prepared by precipitation are mostly earthy powders. They often have a metallic appearance when fused and crystallised.

Heated in air the sulphur is oxidised, while the metal, the sulphate, or the oxide remains. A few sulphides burn, notably those of arsenic and antimony ; the oxide is usually produced, but occasionally the sulphate or the metal,

$$HgS + O_2 = Hg + SO_2$$
$$2CuS + 3O_2 = 2CuO + 2SO_2$$
$$BaS + 2O_2 = BaSO_4.$$

If acids have any action upon them, it results in the liberation of hydrogen sulphide ;

$$ZnS + 2HCl = ZnCl_2 + H_2S.$$

The sulphides of silver, mercury, copper, lead, tin, bismuth and arsenic are attacked only by oxidising agents. All sulphides are harder to dissolve when in their native crystalline condition. Nitric acid, with or without bromine, is the best agent for bringing them into solution. The sulphate, nitrate and free sulphur usually result,

$$CuS + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O + S$$
$$CuS + 8HNO_3 = CuSO_4 + 8NO_2 + 4H_2O.$$

**906. Polysulphides.**—When the sulphide of an alkaline metal or metal of the alkaline earths is digested with sulphur a yellow to dark red solution results.

In these solutions are contained such salts as $Na_2S_3$, $K_2S_5$, $CaS_5$, etc.

These have been thought to be chain compounds, such as

$$Na - S - S - S - S - S - Na,$$

but it is more probable that they have a constitution analogous to that of the sulphates, *e.g.*,

$$Na_2\left[\begin{matrix} S & & S \\ & S & \\ S & & S \end{matrix}\right]$$

The solution of calcium polysulphide is used in horticulture as lime-sulphur wash, which is an efficient destroyer of insect life, fungi, etc.

**907. Hydrogen Persulphides.**—When a solution of calcium polysulphide is slowly poured into an equal volume of ice-cold hydrochloric acid, hydrogen persulphides settle out as a yellow oil.

$$CaS_2 + 2HCl = CaCl_2 + H_2S_2.$$

If the hydrochloric acid is poured into the polysulphide only sulphur is precipitated, for the persulphides are at once decomposed by the excess of alkali surrounding them.

The yellow oil so obtained consists of a mixture of hydrogen disulphide $H_2S_2$ and hydrogen trisulphide $H_2S_3$.

Both soon decompose into sulphur and hydrogen sulphide.

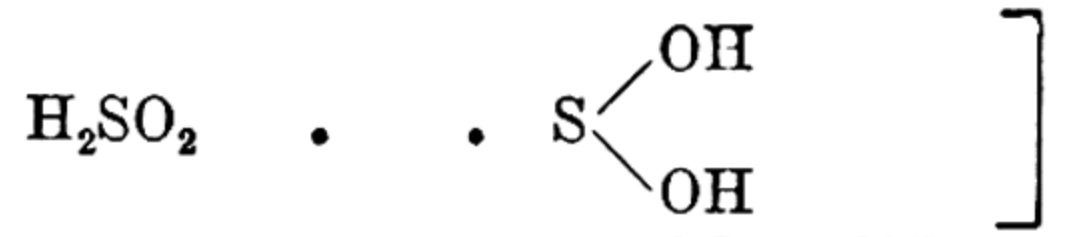
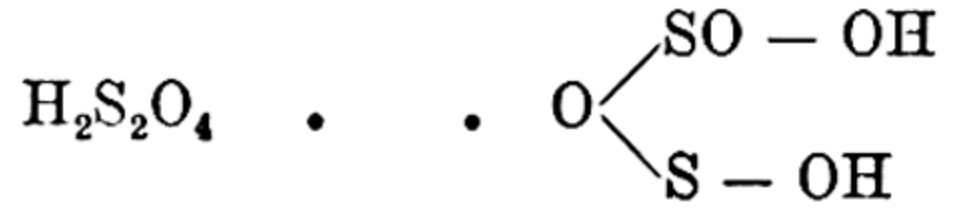
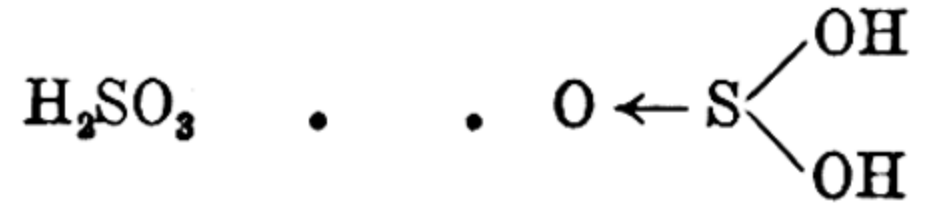
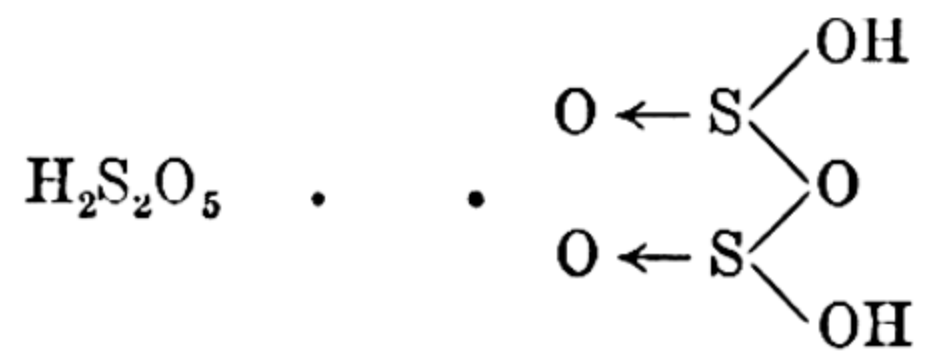
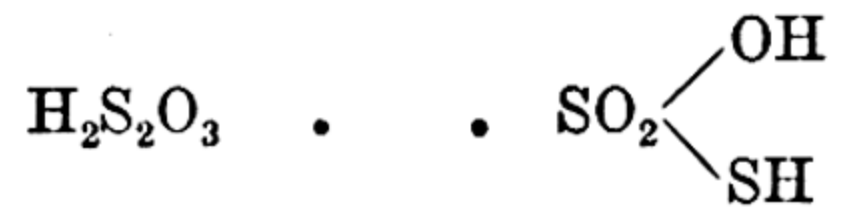
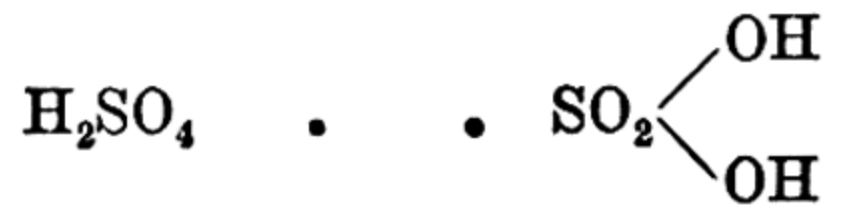
## OXIDES AND OXYACIDS OF SULPHUR

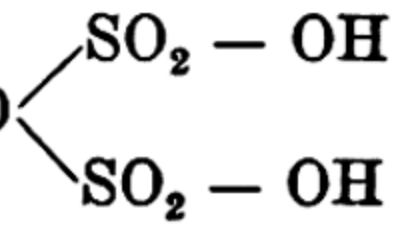
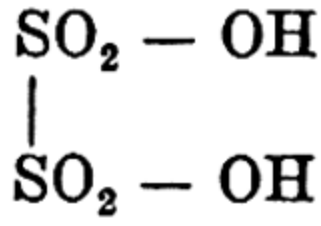
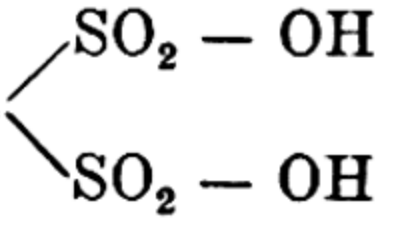
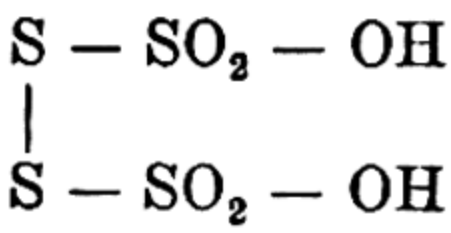
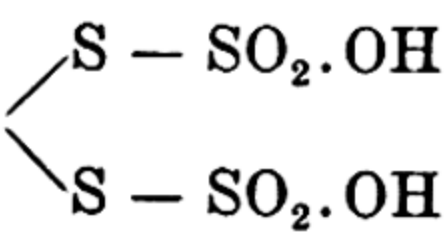
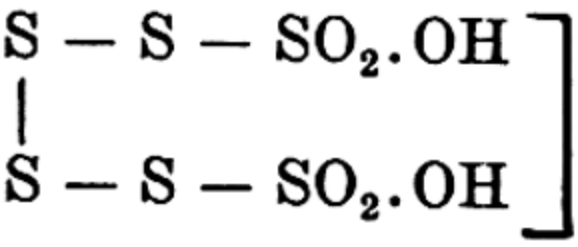
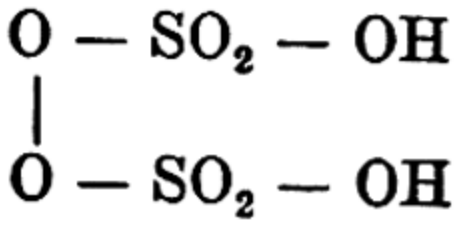
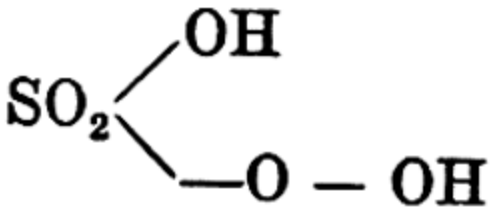
**908. List of Oxides and Oxyacids and Acid Halides of Sulphur.**—There are four oxides of sulphur and a larger number of oxyacids, of which a list is given below :—

### Oxides

| | |
|---|---|
| Sulphur monoxide | $SO$ |
| Sulphur dioxide | $SO_2$ |
| Sulphur sesquioxide | $S_2O_3$ |
| Sulphur trioxide | $SO_3$ |
| Sulphur heptoxide | $S_2O_7$ |
| Sulphur tetroxide | $SO_4$ |

### Oxyacids

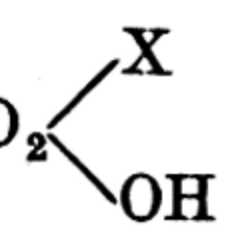
| | | |
|---|---|---|
| [Sulphoxylic acid | $H_2SO_2$ |  ] |
| Hyposulphurous acid | $H_2S_2O_4$ |  |
| Sulphurous acid | $H_2SO_3$ |  |
| Pyrosulphurous acid | $H_2S_2O_5$ |  |
| Thiosulphuric acid | $H_2S_2O_3$ |  |
| Sulphuric acid | $H_2SO_4$ |  |

| | | |
|---|---|---|
| Pyrosulphuric acid | $H_2S_2O_7$ |  |
| Dithionic acid | $H_2S_2O_6$ |  |
| Trithionic acid | $H_2S_3O_6$ |  |
| Tetrathionic acid | $H_2S_4O_6$ |  |
| Pentathionic acid | $H_2S_5O_6$ |  |
| [Hexathionic acid | $H_2S_6O_6$ |  |
| Persulphuric acid | $H_2S_2O_8$ |  |
| Monopersulphuric acid | $H_2SO_5$ |  |

The structural formulæ are those to be assigned to the undissociated acids. The ions may have different structures in some cases. It is not certain whether the co-ordinated linkages depicted by an arrow → are not in fact double bonds =; the point has at present no bearing on the chemical behaviour of these substances.

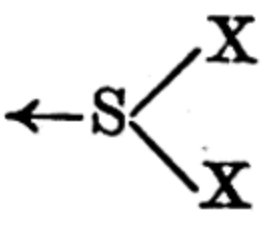
## Halogen Substituted Oxyacids

*Derived from sulphuric acid, of type* $HXSO_3$.

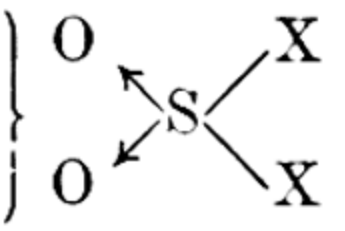
| | | |
|---|---|---|
| Fluorsulphonic acid | $HFSO_3$ |  |
| Chlorsulphonic acid | $HClSO_3$ | |

## Acid Halides

*Derived from sulphurous acid, of type* $SOX_2$.

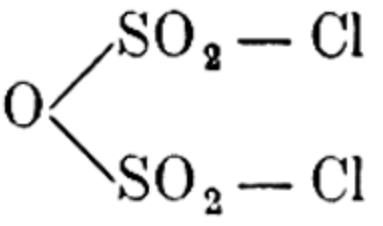
| | | |
|---|---|---|
| Thionyl fluoride | $SOF_2$ |  |
| Thionyl chloride | $SOCl_2$ | |
| Thionyl bromide | $SOBr_2$ | |

*Derived from sulphuric acid, of type* $SO_2X_2$.

Sulphuryl fluoride $SO_2F_2$ . . } 

Sulphuryl Chloride $SO_2Cl_2$ . . }

*Derived from pyrosulphuric acid.*

Pyrosulphuryl chloride $S_2O_5Cl_2$ . . 

## Oxides of Sulphur

**908a. Sulphur Monoxide.**—This oxide is formed by the action of the electric discharge on sulphur dioxide (best mixed with sulphur vapour) at low pressures; also, together with the dioxide, by combustion of sulphur in oxygen at low pressures. It is a colourless gas which decomposes with great ease, particularly in presence of impurities such as water or tap grease. It decomposes completely within a minute at 180° C. It forms sulphur dioxide when sparked with oxygen. With metals it gives sulphides. Alkalis convert it to a liquid which decolorises indigo and may be sodium sulphoxylate.

$$SO + H_2O = H_2SO_2.$$

**909. Sulphur Sesquioxide $S_2O_3$** is obtained by dissolving sulphur in fused sulphur trioxide at 15° C. It forms a bluish-green crystalline substance soluble in sulphuric acid to a blue solution. It readily decomposes into its constituents.

**910. Sulphur Dioxide, Sulphurous Anhydride $SO_2$.**—The fumes evolved by burning sulphur have long been known—as long, certainly, as sulphur itself. The gas was first prepared in a fairly pure state by Priestley, in 1775. Priestley first obtained it, probably mixed with carbon dioxide, by heating olive oil with sulphuric acid (the oil acting as a reducing agent).

**911. Occurrence.**—Sulphur dioxide is found in the gases evolved by volcanoes. The air of towns contains small quantities, chiefly as a result of the burning of iron pyrites contained as an impurity in coal.

**912. Preparation of Sulphur Dioxide.**—Sulphur dioxide may be obtained :—

(1) By burning sulphur in air or oxygen. The gas obtained by burning sulphur in air always, of course, contains nitrogen, but the method is often used industrially.

(2) Sulphur dioxide is often obtained industrially by burning iron pyrites, zinc blende, etc., in air.

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

This is the cheapest way of preparing the gas (*v.* under Sulphuric Acid, § 929), but so prepared, it contains a notable proportion of arsenic. On the large scale the pure gas is prepared from the gases

obtained when pyrites is burned. The gases obtained contain, as a rule, but 6 to 7 per cent. of sulphur dioxide. This is absorbed by water, while the air, etc., passes on ; the gas is then expelled from solution by heat, dried with sulphuric acid and liquefied by pressure. It is sold, as a rule, as the liquid, confined in glass syphons under a pressure of 2–4 atmospheres which evolve about 500 litres of gas. The use of these is so convenient that the laboratory preparation of the gas is rarely carried out.

(3) Sulphur dioxide is prepared by the action of hot concentrated sulphuric acid on a reducing agent, mercury, copper or other metal, sulphur, charcoal, etc. (§ 936). Copper is commonly employed. The main reaction is

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2,$$

but copper sulphide is simultaneously formed. The apparatus shown in Fig. 173 may be employed. The acid has to be heated above 100° C. before any gas comes off, and the temperature should not be allowed to rise too much or the action may become violent.

The gas so obtained contains sulphur trioxide, sulphuric acid vapour, etc., and is purified by passing it through a little water and then drying it with sulphuric acid.

The gas may be collected by downward displacement or over mercury.

(4) The action of moderately diluted sulphuric acid (1 : 1) on a sulphite (preferably sodium bisulphite) may be employed.

$$H_2SO_4 + NaHSO_3 = NaHSO_4 + H_2O + SO_2.$$

The gas is dried by sulphuric acid.

**913. Formula.**—When sulphur burns in oxygen there is no change in the volume of the gas. So 1 volume sulphur dioxide contains 1 volume of oxygen, and 1 *molecule* sulphur dioxide must contain 1 *molecule* oxygen. The formula must then be $S_nO_2$. Since the molecular weight, obtained from the vapour density, is 64, the molecular weight of sulphur contained therein is $64 - 2 \times 16 = 32$, 1 atom of sulphur. The formula is accordingly $SO_2$.

**914. Properties.**—Sulphur dioxide is a colourless gas with the choking smell characteristic of burning sulphur and a characteristic taste. It is poisonous and has been much used for destroying low forms of life by fumigation with sulphur. It is now largely superseded for this purpose by formaldehyde, which is not destructive to fabrics, etc. Sulphur dioxide is considerably heavier than air (D. = 2·26 referred to air, 32 referred to hydrogen). It is readily liquefied by a pressure of 2–4 atmospheres at the ordinary temperature. The liquid is colourless and boils at — 10° C. A good

freezing mixture will therefore condense the gas. The liquid is a good solvent and resembles water in that it dissolves salts, which dissociate electrolytically in solution in it. Sulphur dioxide is very soluble in water. At 0° C. 1 volume of water dissolves 79·79 volumes of the gas ; at 20° C., 39·37 vols.

**915. Chemical Properties.**—Sulphur dioxide is decomposed when heated to a high temperature, sulphur trioxide and sulphur resulting,

$$3SO_2 \rightleftharpoons 2SO_3 + S.$$

It is also decomposed by light, a white cloud of sulphur trioxide being formed when a beam of sunlight passes through a long tube containing the gas. An electrical discharge at low pressures converts it into sulphur monoxide (§ 908A).

Sulphur dioxide reacts reversibly with oxygen when heated, especially in presence of certain catalysts, notably metallic platinum (§ 918). $2SO_2 + O_2 \rightleftharpoons 2SO_3$.

With chlorine it reacts to form sulphuryl chloride $SO_2Cl_2$, the reaction being catalysed by camphor. With fluorine and bromine similar reactions take place.

Certain of the metals react with the gas. Thus red-hot finely-divided iron absorbs it, forming iron sulphide and oxide,

$$3Fe + SO_2 = 2FeO + FeS.$$

Potassium burns in the gas, forming the sulphite and thiosulphate,

$$4K + 3SO_2 = K_2S_2O_3 + K_2SO_3.$$

With water, sulphur dioxide forms sulphurous acid,

$$H_2O + SO_2 \rightleftharpoons H_2SO_3.$$

The presence of this acid, which cannot be isolated free from water, is demonstrated :—

(1) By the failure of sulphur dioxide to follow Henry's law (*v.* § 564).

(2) By the solution exhibiting the properties of an acid, *e.g.*, good conductivity, effect on indicators, reaction with metals, oxides, etc., to form salts.

Sulphur dioxide reacts vigorously with such basic oxides as lime, forming sulphites, $CaO + SO_2 = CaSO_3$.

Lead dioxide reacts vigorously with it, oxidising it and forming lead sulphate, $PbO_2 + SO_2 = PbSO_4$.

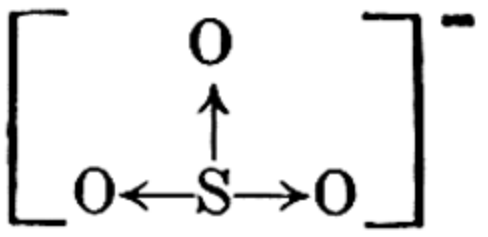
The reducing action of sulphur dioxide is chiefly manifest in solution. If is therefore discussed under sulphurous acid.

**916. Sulphurous Acid** smells strongly and tastes of sulphur dioxide, which is present,

$$H_2O + SO_2 \rightleftharpoons H_2SO_3,$$

in its solutions. The action of heat or evaporation decomposes the acid, for it causes the dissolved uncombined sulphur dioxide to escape; more sulphurous acid then decomposes and restores the equilibrium and this process continues until nothing but water remains.

The structural formulæ of sulphurous acid and the sulphites have occasioned a good deal of dispute. The ion is almost certainly

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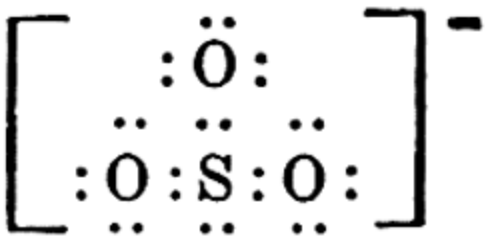
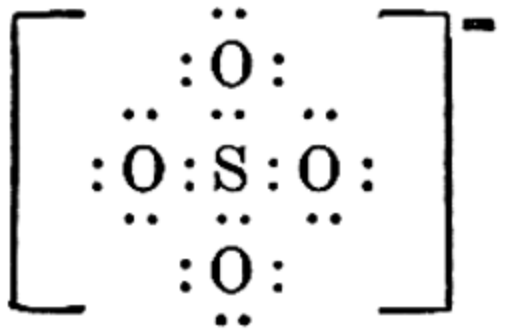



This structure is supported by the ready attachment of an oxygen or sulphur atom forming the sulphate or thiosulphate ions

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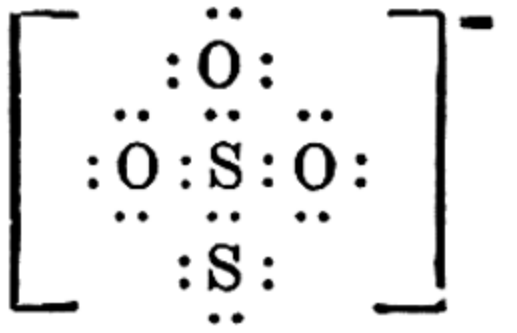
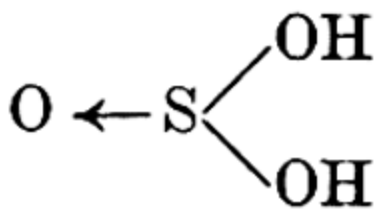
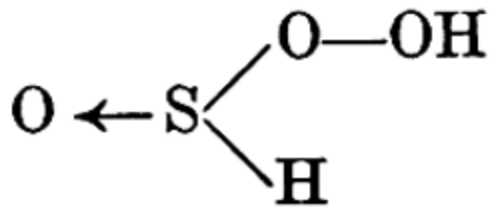



The structure of the undissociated acid is less certain. The sulphur atom is probably quadrivalent as in sulphur dioxide, but may be sexivalent. The formulæ




(1)

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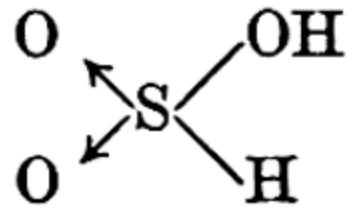
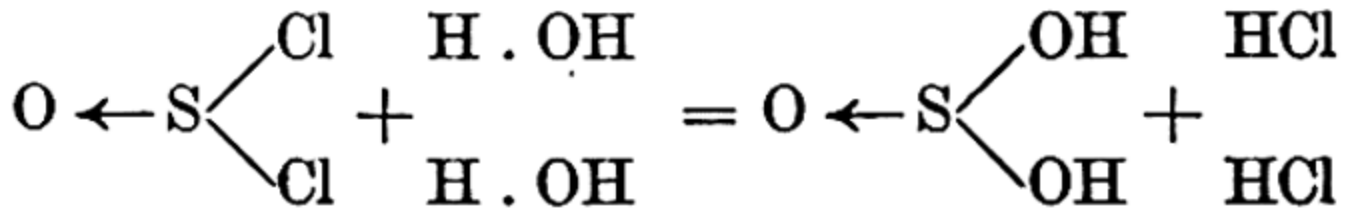


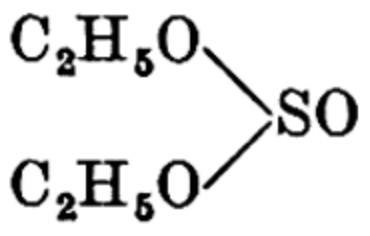

(3)

are three of the most probable.

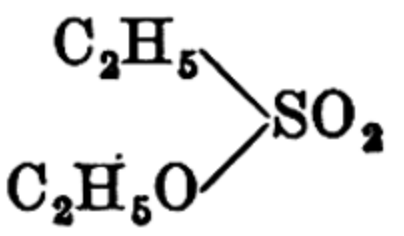
Formula (1) is indicated by the formation of the acid from thionyl chloride and water,



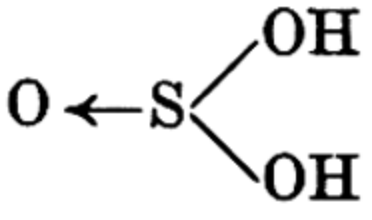

and explains all the properties of the acid very well, except the fact that two diethyl sulphites exist. These probably have the formula




and




The latter formula would indicate the acid to have formula (2) or (3). The esters are not, however, a reliable guide and the formulæ




may be adopted with reasonable confidence. Some

years ago it was announced that two different sodium potassium sulphites $NaKSO_3$ and $KNaSO_3$, existed. This would necessitate formula (2) or (3), but the real existence of these isomeric sulphites has not been substantiated.

Sulphurous acid is a strong reducing agent, being readily oxidised to sulphuric acid. In air it is slowly oxidised,

$$2H_2SO_3 + O_2 = 2H_2SO_4.$$

Sulphurous acid reacts with the halogens to form sulphuric acid,

$$H_2SO_3 + Cl_2 + H_2O = H_2SO_4 + 2HCl.$$

Thus solutions of sulphurous acid may be titrated with iodine. The sulphurous acid should run into the iodine, not *vice versa*, because in the latter case the by-reaction

$$SO_2 + 4HI = 2I_2 + 2H_2O + S$$

also takes place.

It reduces ferric salts to ferrous salts,

$$2FeCl_3 + H_2SO_3 + H_2O = 2FeCl_2 + 2HCl + H_2SO_4.$$

Iodates are reduced to iodine,

$$2KIO_3 + 5H_2SO_3 = I_2 + 2KHSO_4 + 3H_2SO_4 + H_2O.$$

This affords a delicate test for sulphur dioxide. Papers impregnated with a solution of potassium iodate [1] and starch turn blue when only traces of sulphur dioxide are present. The reaction of solutions of iodates and sulphurous acid affords a good example of a time-reaction (§ 1102).

A simple test for sulphurous acid or sulphur dioxide is to add the solution to, or pass the gas through, a neutral dilute solution of potassium permanganate. This is at once decolorised,

$$2KMnO_4 + 5H_2SO_3 = 2KHSO_4 + 2MnSO_4 + H_2SO_4 + 3H_2O$$

and the colourless liquid gives the barium chloride reactions characteristic of a sulphate (§ 937). The latter part of the test is necessary, as other reducing agents may decolorise permanganates.

The reaction of sulphurous acid and hydrogen sulphide (§ 901) is an example of sulphurous acid or sulphur dioxide acting as an oxidising agent in presence of the stronger reducing agent, hydrogen sulphide.

Sulphur dioxide, in presence of moisture, *i.e.*, sulphurous acid, acts as an efficient bleaching agent, which is the more valuable in that, unlike chlorine (the other chief bleaching agent), it does not affect the strength of the materials bleached. Cotton and linen fibre are

[1] Do not confuse with starch—potassium *iodide* papers (§ 1050).

ordinarily bleached with chlorine, but the tenderer materials, wool and silk,[1] are bleached with sulphur dioxide. The use of sulphur fumes for bleaching was known to the Romans. The principle of the method is the reduction of the colouring matter to a colourless *leuco*-compound,

$$H_2SO_3 + H_2O + X = H_2SO_4 + H_2X.$$

An actual example is the bleaching of woollen goods. The materials are well washed and while still wet are hung in a chamber in which sulphur dioxide is made by burning sulphur. The same method is employed for bleaching silk, straw, sponges, etc.

The colouring matter is only reduced, not profoundly altered, and consequently it is not uncommon for the colour to reappear in consequence of oxidation by air and light. The yellow colour of old straw hats, flannel trousers, newspapers, etc., is due to this action of air and light.

**917. The Sulphites.**—The sulphites of the alkali metals and of the alkaline earths are salts of some importance.

Three series of salts have been obtained,

Bisulphites, *e.g.*, $NaHSO_3$, $Ca(HSO_3)_2$.
Normal sulphites, *e.g.*, $K_2SO_3$, $BaSO_3$.
Metabisulphites (pyrosulphites), *e.g.*, $Na_2S_2O_5$.

The normal sulphites are stable salts, odourless in solution. When treated with acids they give sulphurous acid, which decomposes to sulphur dioxide,

$$Na_2SO_3 + 2H_2SO_4 = 2NaHSO_4 + H_2O + SO_2.$$

This is evolved if the acid used is concentrated. Sulphites give, with barium chloride, a white precipitate of barium sulphite, $BaSO_3$, but this is soluble in dilute hydrochloric acid, therein differing from barium sulphate.

The sulphites have the reducing properties of sulphurous acid, forming sulphates with oxidising agents. They are detected (*a*) by their giving sulphur dioxide with hot dilute sulphuric acid; (*b*) by their reducing permanganates acidified with dilute hydrochloric acid and forming sulphates, detected by the barium sulphate test.

Those of the sulphites which have any practical importance are mentioned under the heading of the element in question.

**918. Sulphur Trioxide, Sulphuric Anhydride $SO_3$.**—Sulphur trioxide has been known since the seventeenth century, when it was prepared by distilling anhydrous ferric sulphate,

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

[1] Hy-drogen peroxide is often used for goods of the finest class.

*Preparation.*—Sulphur trioxide is prepared—

(1) By distillation of sulphuric acid with excess of phosphorus pentoxide, $P_2O_5 + H_2SO_4 = 2HPO_3 + SO_3$.

(2) By distillation of ferric and other sulphates (*v. supra*).

(3) By the direct union of sulphur dioxide and oxygen,

$$2SO_2 + O_2 \rightleftharpoons 2SO_3.$$

The details of this process and the theory of the equilibrium between sulphur dioxide and oxygen is discussed under the contact process for the manufacture of sulphuric acid (§ 930). This reaction is very slow in absence of a catalyst, but in presence of platinum it is rapid and complete at about 400° C. The apparatus illustrated may be

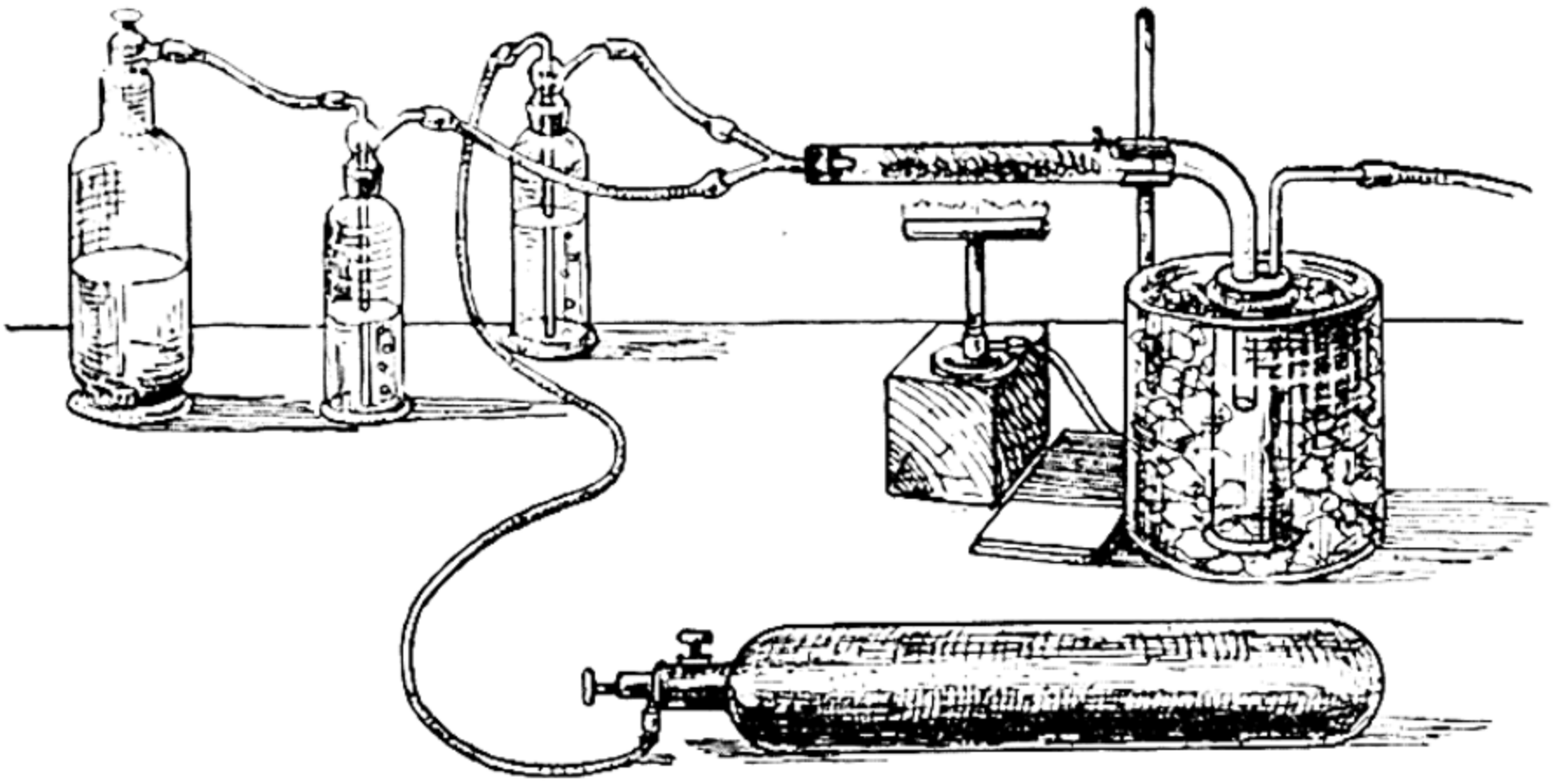


Fig. 169.—Preparation of sulphur trioxide.

used for its preparation in the laboratory. Sulphur dioxide from a syphon and oxygen from a cylinder pass through wash bottles containing sulphuric acid, the rate of flow being adjusted to about 2 parts of the former to 1 of the latter. The gases then pass through a tube containing platinised asbestos heated to 400° C. (the temperature being regulated preferably by enclosing the tube in some form of hot-air jacket). White clouds of sulphur trioxide come over and may be condensed in a cooled receiver.

**919. Properties.**—Sulphur trioxide exists in three modifications:

α-sulphur trioxide, which forms colourless ice-like needles. M.P. 16·8° C. B.P., 44·9° C.

β-sulphur trioxide forms silky asbestos-like needles, which melt at 32·5C°.

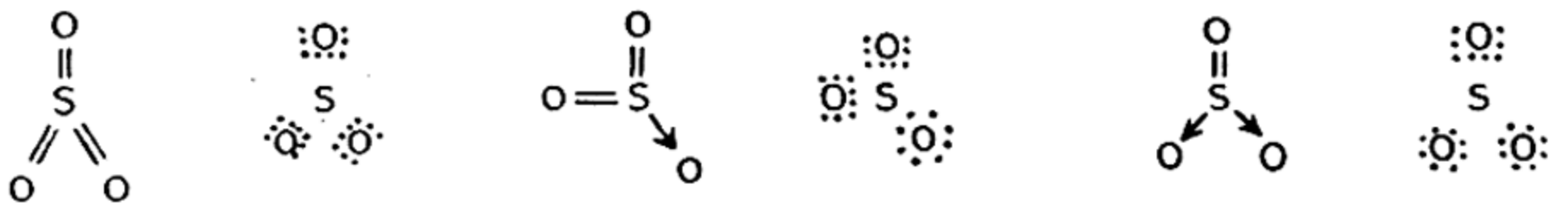
γ-sulphur trioxide, also a silky asbestos-like form which is obtained by very complete drying of β-sulphur trioxide. It melts at 62·2° C. under 1,743 mm. pressure, but sublimes without melting at ordinary pressures. The question of the relationships of these forms is not clearly settled. It seems that β-sulphur trioxide may be itself a mixture of two 'asbestos-like' forms.

Sulphur trioxide when heated decomposes in accordance with the equation $2SO_3 \rightleftharpoons 2SO_2 + O_2$. It is a typical acidic oxide and the solid combines with water with almost explosive violence, forming sulphuric acid, $SO_3 + H_2O = H_2SO_4$. It combines also with basic oxides, producing sulphates,

$$CaO + SO_3 = CaSO_4.$$

It forms curious addition products with many elements, such as $I_2(SO_3)_6$, $TeSO_3$.

The structure of the sulphur trioxide molecule is not certain. It may be I. giving sulphur a total valency group of twelve electrons as in $SF_6$; or II.



I II III

giving sulphur a valency of four and valency group of 10 electrons; or III. with a valency of two and a valency group of 8 electrons. The second formula is perhaps the most likely.

**920. Sulphur Heptoxide $S_2O_7$** is formed by the action of the silent electric discharge on a mixture of sulphur dioxide and oxygen. It slowly decomposes into sulphur trioxide and oxygen. With water sulphuric acid and oxygen are formed,

$$2S_2O_7 + 4H_2O = 4H_2SO_4 + O_2.$$

**920a. Sulphur Tetroxide $SO_4$** is formed by the action of the glow-discharge on a mixture of sulphur dioxide and oxygen (1 : 10). It is a white solid which decomposes above — 5° C. to sulphur heptoxide and oxygen.

### Oxyacids of Sulphur

**921. Sulphoxylic Acid $H_2SO_2$.**—This acid is not known in the free condition. Organic derivatives of it, however, exist. Sodium sulphoxylate is said to have been produced by the action of sodium ethylate on sulphur sesquioxide, and by the action of aqueous alkalis on sulphur monoxide. There is a good deal of doubt, however, as to the identity of the salts so produced.

**922. Hyposulphurous Acid (Hydrosulphurous Acid) $H_2S_2O_4$.**—When certain metals, for example zinc, dissolve in sulphurous acid, no hydrogen is evolved, and instead of a sulphite a hyposulphite is formed.

$$Zn + 2SO_2 = ZnS_2O_4.$$

Hyposulphites are also prepared by the action of concentrated sodium bisulphite solution on zinc dust, sulphur dioxide being passed through the liquid,

$$2NaHSO_3 + SO_2 + Zn = Na_2S_2O_4 + ZnSO_3 + H_2O.$$

The solution is treated with lime, which precipitates the zinc as hydroxide, which is filtered off. The filtrate is saturated with common salt, which diminishes the solubility of the sodium hyposulphite so much that it crystallises.

The free acid is obtained by treating calcium hyposulphite with oxalic acid. It forms a yellow solution. This solution absorbs oxygen from the air, forming

thiosulphuric acid, which soon decomposes into sulphur dioxide and sulphur.

The *hyposulphites* (hydrosulphites) are of commercial importance as reducing agents for indigo-dyeing. They reduce copper, silver and gold salts to the metal, even reducing copper salts to copper hydride $CuH_2$. Air quickly oxidises them to metabisulphites.

$$2Na_2S_2O_4 + O_2 = 2Na_2S_2O_5.$$

**923. Sodium Hyposulphite** is made on the large scale by the action of zinc on sodium bisulphite as described above. It is valuable for 'stripping' dyes, *i.e.*, bleaching dyed fabrics by its intense reducing action, and also for converting indigo into indigo-white, the soluble compound used in indigo dyeing.

The properties of a hyposulphite may be demonstrated by preparing a concentrated solution of sulphur dioxide and adding to it granulated zinc, stirring from time to time. After a quarter of an hour the solution will be found to reduce 'indigo sulphate' to the colourless reduction product.

The name sodium hyposulphite was at one time applied to sodium thiosulphate. The substance which photographers buy and sell as 'hypo' is sodium thiosulphate and not what the chemist now calls sodium hyposulphite.

**924. Thiosulphuric Acid and the Thiosulphates.**—Thiosulphuric acid is unstable, but the thiosulphates are of considerable commercial importance.

The thiosulphates are made :—

(1) By boiling solutions of sulphites with sulphur. This is the method practically adopted,

$$Na_2SO_3 + S = Na_2S_2O_3.$$

The preparation may be carried out by dissolving 50 gms. of crystallised sodium sulphite in 100 c.c. of water and adding 7 gms. of finely-ground roll-sulphur (not flowers of sulphur, which contain the unreactive amorphous form). The mixture is gently boiled for about two hours, water being replenished as it evaporates. When the sulphur has disappeared, the hot solution is filtered and evaporated till a specimen crystallises when cooled and seeded with a minute crystal of the thiosulphate.

(2) By the action of caustic alkalis on sulphur (§ 894).

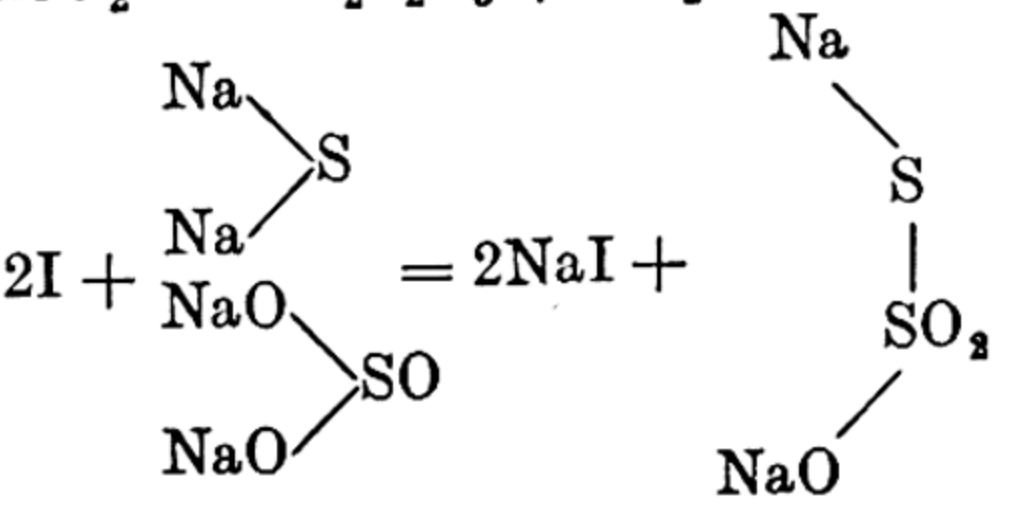
(3) By the oxidation of soluble sulphides in air,

$$2K_2S_2 + 3O_2 = 2K_2S_2O_3$$
$$2K_2S_5 + 3O_2 = 2K_2S_2O_3 + 6S.$$

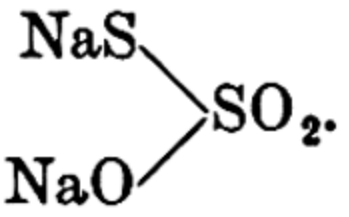
(4) On the industrial scale crude sodium sulphide, which contains some carbonate, is heated with sulphur dioxide,

$$2Na_2S + Na_2CO_3 + 4SO_2 = 3Na_2S_2O_3 + CO_2$$

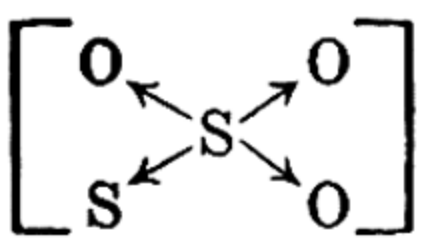
(5) Iodine reacts with an equimolecular mixture of sodium sulphide and sulphite, yielding the thiosulphate. This reaction gives us the key to their structure,



We accordingly write the formula of sodium thiosulphate as




This formula would be that of the undissociated salt (if it exists); the thiosulphate ion is to be regarded as

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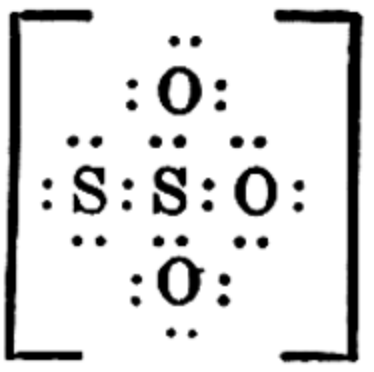
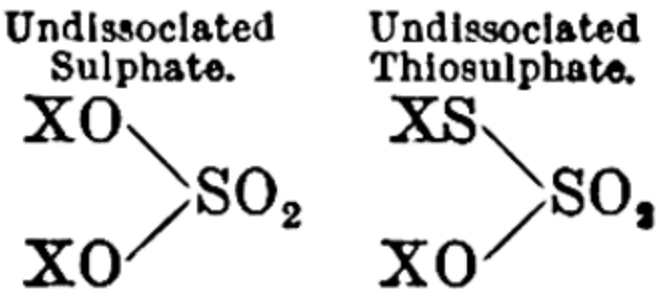



Thiosulphuric acid is structurally analogous to the sulphuric acid, one oxygen atom being replaced by a sulphur atom.

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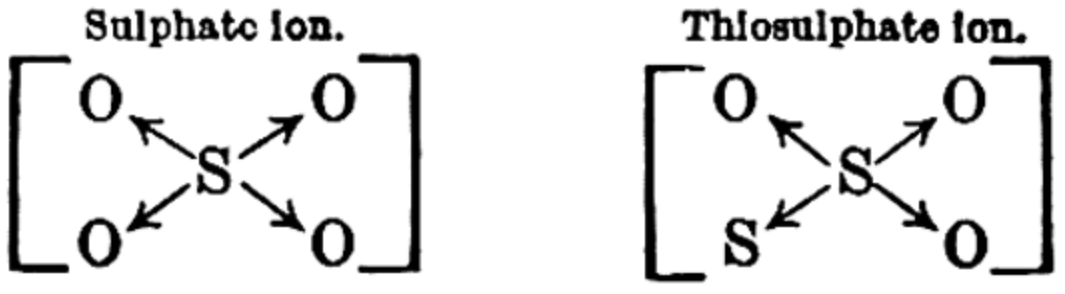



Thiosulphuric acid is obtained by the action of acids upon a thiosulphate. It decomposes after a short delay to sulphurous acid and sulphur,

$$H_2S_2O_3 = H_2SO_3 + S.$$

The delay is due to the formation of a complex of sulphur and polythionate. As the latter gradually splits up the complex becomes less soluble and finally precipitates. The thiosulphates crystallise well and are mostly soluble. When heated they decompose into polysulphides and sulphates,

$$4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5.$$

The thiosulphates of the heavy metals decompose even when boiled in solution into sulphides, sulphur, sulphates, etc.

Mild oxidising agents, such as iodine or ferric chloride, convert them into tetrathionates,

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$
$$2Na_2S_2O_3 + 2FeCl_3 = 2FeCl_2 + 2NaCl + Na_2S_4O_6.$$

The reaction with iodine is used to estimate that element (§ 1090).

The action of strong oxidising agents, such as chlorine and bromine, ultimately produces the sulphate and sulphuric acid,

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O = Na_2SO_4 + H_2SO_4 + 8HCl.$$

The thiosulphates readily form *double salts* and complex ions, of which the most notable are the double sodium silver thiosulphates, which find a use in the fixing of photographs (§ 318).

## Sulphuric Acid

**925. Historical.**—Sulphuric acid was not known to the ancients, and it seems to have been first mentioned in the Latin works attributed to Geber. If we believe that these are the actual work of Jabir ibn Hayyan we should place its discovery in the ninth century A.D.; if, on the other hand, we believe, as most scholars do, that these Latin works are much later, we should place the discovery about the twelfth or thirteenth century. It was first made by the distillation of alum, but later and more commonly by distilling ferrous sulphate, 'green vitriol.' The name *oil of vitriol* derives from this method of preparation. The equation for this process is

$$2FeSO_4 . 7H_2O = Fe_2O_3 + SO_2 + H_2SO_4 + 13H_2O.$$

Later sulphuric acid was prepared by burning a mixture of sulphur and nitre under a bell-jar containing a little water. Most of the sulphur burnt to the dioxide but some trioxide was formed, and this with the water produced sulphuric acid. This process was gradually developed into the *lead chamber* process for the manufacture of the acid.

The manufacture of sulphuric acid is to-day an enormous industry, for in 1925 rather over 10,000,000 tons of the acid were produced.

**926. Occurrence.**—Free sulphuric acid is not uncommonly found in mineral springs. It derives from the oxidation of pyrites in presence of air and moisture.

$$2FeS_2 + 2H_2O + 7O_2 = 2H_2SO_4 + 2FeSO_4.$$

The waters of a Spanish river, the Rio Tinto, which rises from sources rich in pyrites, contain notable quantities of the acid together with ferrous and copper sulphates.

**927. Preparation.**—Sulphuric acid is never prepared in the laboratory. Its preparation is not particularly easy, and acid of high purity is purchasable at a low price.

Before discussing the methods of manufacture, it may be well to give a list of some of the reactions which are capable of producing the acid.

Sulphuric acid is formed :—

(i.) When sulphur trioxide combines with water.

$$SO_3 + H_2O = H_2SO_4.$$

(ii.) When hydrated sulphates are decomposed by heat (§ 938),

$$Al_2(SO_4)_3 . 18H_2O = Al_2O_3 + 3H_2SO_4 + 15H_2O.$$

(iii.) When sulphates are decomposed by heating them with a non-volatile acidic oxide (*e.g.*, silica), sulphur trioxide is formed,

$$CaSO_4 + SiO_2 = CaSiO_3 + SO_3,$$

which may be made to combine with water.

(iv.) The sufficiently vigorous oxidation of sulphur yields the acid (§ 894).

(v.) The oxidation of sulphurous acid by almost any oxidising agent yields sulphuric acid (§ 916).

(vi.) By the action of sulphuryl chloride or chlorsulphonic acid on water,

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$
$$HSO_3Cl + H_2O = H_2SO_4 + HCl.$$

**928. Manufacture of Sulphuric Acid.**—The vast bulk of the world's sulphuric acid is made by oxidising sulphur dioxide by the Lead Chamber process (§ 929) or the Contact process (§ 930). The former produces about two-thirds of the acid manufactured in Great Britain. The reaction of calcium sulphate with sand or clay ( (iii.) above) has been used, but not on an extended scale.

**929. The Lead Chamber Process.**—The reactions on which the lead chamber process depends are still somewhat in doubt, but the process is, essentially, as follows :—

(1) A mixture of sulphur dioxide and air is produced by burning sulphur or iron pyrites,

$$S + O_2 = SO_2$$
$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

(2) The gases so produced are mixed in large reaction chambers with a small proportion of oxides of nitrogen in the presence of water in the form of fine sprays. It is probable that the nitrogen peroxide oxidises the sulphur dioxide to the trioxide,

$$(a)\ SO_2 + NO_2 = SO_3 + NO,$$

and that this then forms sulphuric acid, which falls to the bottom of the reaction chambers,

$$(b)\ SO_3 + H_2O = H_2SO_4,$$

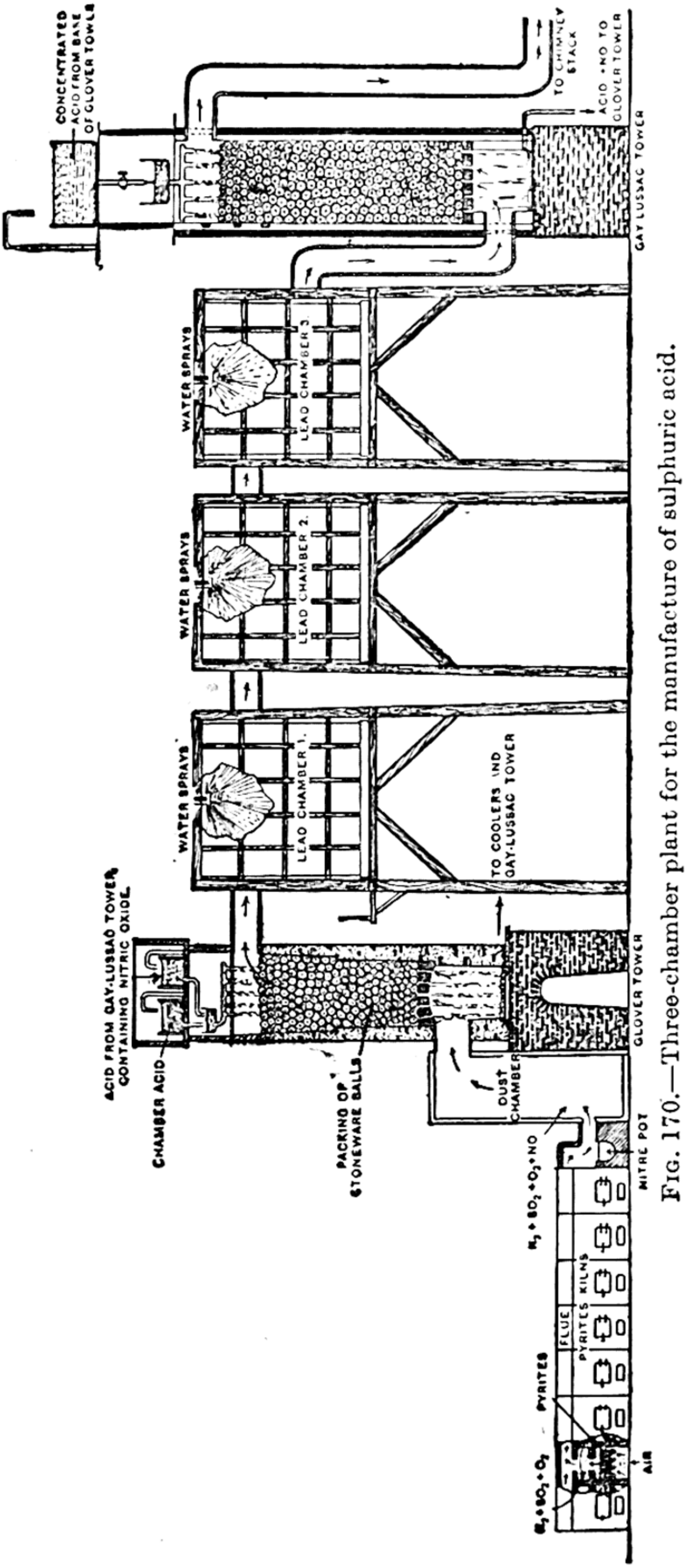



FIG. 170.—Three-chamber plant for the manufacture of sulphuric acid.

while the nitric oxide formed is reoxidised to nitrogen peroxide, which again oxidises more sulphur dioxide,

$$2NO + O_2 = 2NO_2.$$

The nitrogen oxides act as a carrier of oxygen to the sulphur dioxide. They are not used up but are swept out of the chamber by the nitrogen of the air which was supplied to burn the sulphur or pyrites and to oxidise the sulphur dioxide.

(3) The nitrogen oxides are removed from the issuing gases by absorption in sulphuric acid and then returned to the chambers.

This simple theory is not everywhere accepted, for it is often believed that an intermediate compound is formed. It is true that if water is deficient, chamber crystals or nitrosyl sulphate

$$[NO]^+HSO_4^-$$

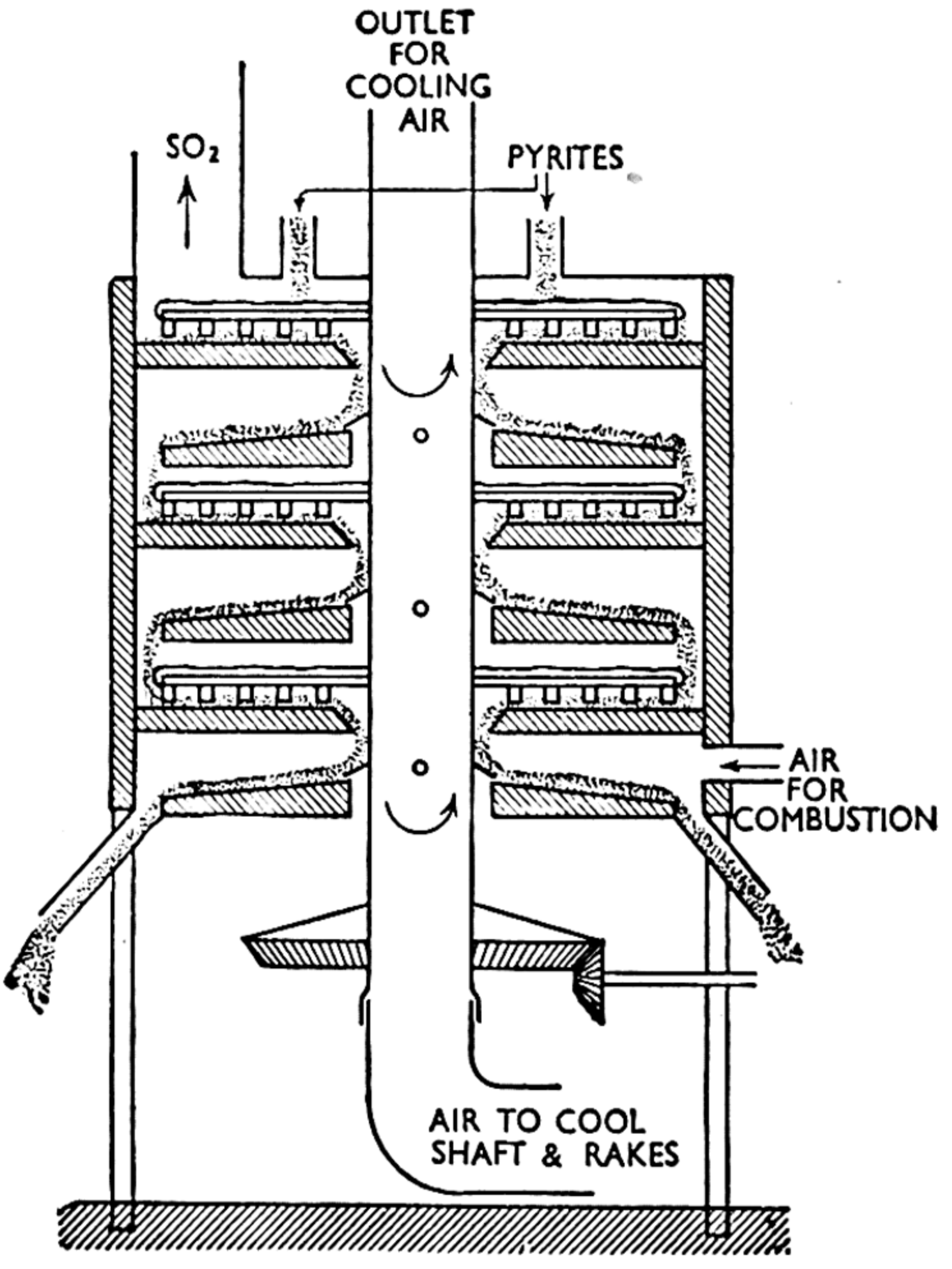



Fig. 170a.—Pyrites burner.

are formed, which water decomposes into sulphuric acid and oxides of nitrogen. Others believe that nitroxysulphuric acid, $H_2N_2SO_6$, is formed as an intermediate compound, but it does not, on the whole, appear necessary to assume any set of reactions more complicated than those detailed above.

Fig. 170 shows a diagram of the plant used for the manufacture of sulphuric acid by the lead chamber process.

Iron pyrites, broken into lumps, may be burned on grates, the air supply being so regulated that a mixture of nitrogen, sulphur dioxide and oxygen passes into the flue above the kilns,

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

In modern practice, 'smalls,' *i.e.*, powdered or crushed pyrites, may be burnt in a mechanical furnace (Fig. 170a), in which rotating rakes stir the mass so as to expose it to air. Instead of iron pyrites, sulphur, spent oxide from the gasworks (§ 551), zinc blende (§ 405), etc., may be used.

The mixture of gases is then led over the nitre-pot, in which a mixture of sodium nitrate and sulphuric acid slowly evolves nitric acid vapour. This is reduced to nitrogen peroxide by the sulphur dioxide.

In place of the nitre-pot, most works now use an arrangement for oxidising ammonia catalytically with platinum gauze (§ 738).

The gases then pass into a dust chamber, which is very necessary if 'smalls' is burnt, but is omitted if lump pyrites or sulphur is used as the source of sulphur dioxide. The gases now pass into the Glover tower, which is built of acid-proof material, 'volvic lava,' lined outside with lead. The tower is packed with acid-proof stoneware balls (or sometimes with flints or lumps of quartz). Down this tower flows sulphuric acid, containing dissolved nitric oxide, taken from the base of the Gay-Lussac tower, the function of which will be seen later. The hot gases at 300–500° C. expel the nitric oxide from the acid and carry the nitric oxide on into the lead chambers. This is oxidised by the oxygen in the gases to nitrogen peroxide.

Some 'chamber acid' (*c.* 60 per cent.) is often run down the Glover tower in order to concentrate it, thus utilising the waste heat of the uprising gases.

The gases now pass through two or three lead chambers, each containing up to 50,000 cubic feet of gas. These are built of very pure lead in order to minimise corrosion, and are suspended from a wooden framework. In modern practice, space is saved by using large water-cooled vertical towers 45 feet high and 22 feet in diameter. Like the chambers, these must be constructed of pure lead.

In the chambers the gases meet with fine sprays of water projected from the roofs, and the reactions, already mentioned at the beginning of this section, produce sulphuric acid and nitric oxide,

$$NO_2 + SO_2 + H_2O = H_2SO_4 + NO,$$

and the nitric oxide is again oxidised to nitrogen peroxide,

$$2NO + O_2 = 2NO_2,$$

and the cycle of reactions is repeated until no sulphur dioxide remains. The gases, now consisting of nitrogen and nitric oxide, enter the Gay-Lussac tower, of construction similar to, though less robust than, the Glover tower. Down the Gay-Lussac tower trickles strong acid taken from the bottom of the Glover tower. This dissolves the nitric oxide, leaving only nitrogen to pass out to the chimney, which provides the draught which is the motive power of the gases. The acid, containing dissolved nitric oxide, is pumped to the top of the Glover tower.

The acid which accumulates on the floor of the chambers contains 60–65 per cent. $H_2SO_4$, and is either sold as such to manufacturers of superphosphate (§ 372), ammonium sulphate (§ 690), nitric acid (§ 735), sodium carbonate (§ 235), etc., or, alternatively, is concentrated, usually by evaporating it in pans made of a special alloy of iron and silicon.

The contact process makes such good and pure concentrated acid, that the chamber process tends to specialise in the manufacture of the 60 to 65 per cent. acid for purposes where a cheap acid of this concentration and not of special purity is satisfactory.

**930. The Contact Process.**—When a mixture of sulphur dioxide and oxygen is heated the gases combine to some extent, forming sulphur trioxide,

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 22{,}600 \text{ cals.}$$

Since this reaction evolves heat, it follows, from the principle of Le Chatelier, that at high temperatures the yield of sulphur trioxide will be diminished. It is therefore desirable, in order to get the best possible yield, to work at a fairly low temperature. The rate of reaction is, however, very small if no catalyst is used. Platinum is, however, a very efficient catalyst, and it is found that, using platinised asbestos as a catalyst, practically 100 per cent. combination of sulphur dioxide and oxygen can be quickly obtained at 400–450° C. At lower temperatures the reaction is too slow, though in time a good yield is obtained, and at higher temperatures the maximum percentage of the gases which can be transformed into sulphur trioxide diminishes and above 1,000° C. becomes practically zero.

The process then is as follows :—

(1) A pure mixture of air and sulphur dioxide, free from dust, arsenic, chlorine and water, is prepared. The impurities mentioned ' poison ' the catalyst, *i.e.*, destroy its activity.

(2) The mixture is passed over platinised asbestos or some form of finely-divided platinum, the temperature being kept near 450-500° C. The gases form sulphur trioxide,

$$2SO_2 + O_2 \rightleftharpoons 2SO_3.$$

(3) The sulphur trioxide obtained is absorbed in concentrated sulphuric acid, to which water is added in a quantity so regulated that it just converts the sulphur trioxide into sulphuric acid,

$$SO_3 + H_2O = H_2SO_4.$$

The process is carried out by burning sulphur, or iron pyrites as in the chamber process. The gas is then cooled and thoroughly freed from dust by forcing it through scrubbers packed with quartz. It is then washed with dilute caustic soda (insufficient, of course, in quantity to absorb any serious quantity of sulphur dioxide). These processes remove all dust and arsenic very efficiently, and on this removal depends the success of the process, for both dust and arsenic clog and ' poison ' the platinum catalyst, rendering it useless after some time.

Other substances than platinum can catalyse the reaction of sulphur dioxide and oxygen. In the U.S.A. nearly half the contact acid is manufactured by passing the mixed gases over vanadium pentoxide. Iron oxide has also been used as catalyst.

The gases (usually $N_2$, 83 per cent. ; $O_2$, 10 per cent. ; $SO_2$, 7 per cent.) then pass through a heat exchanger (Fig. 171), wherein they

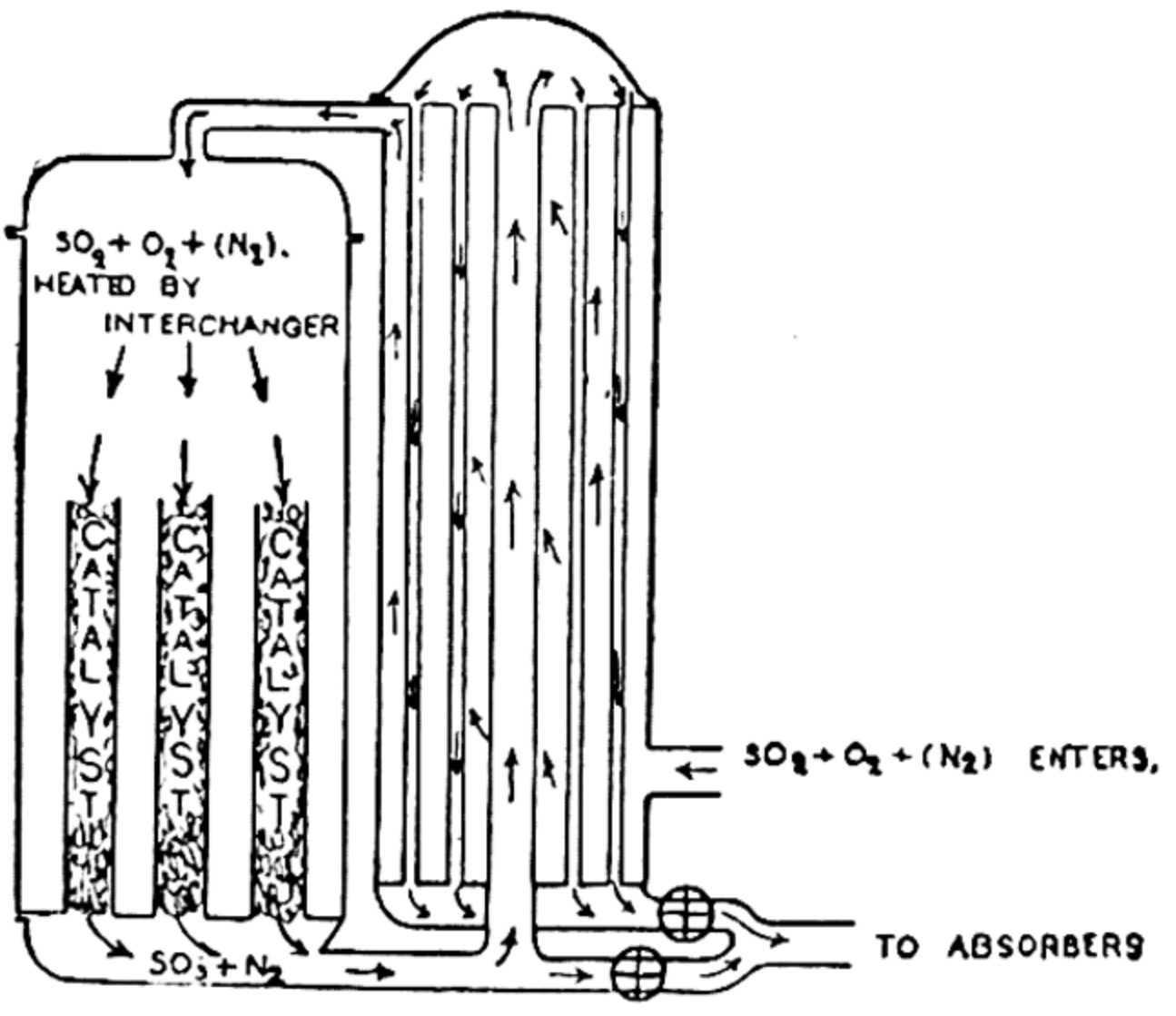



FIG. 171.—Tentelew converter for manufacture of sulphur trioxide.

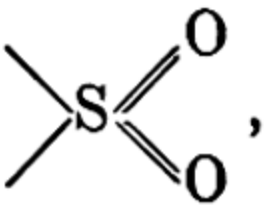
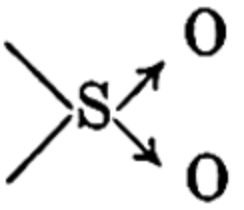
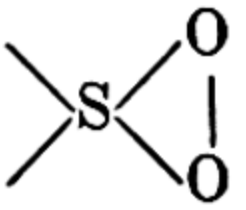
are heated up to the optimum reaction temperature (400–450° C.) by the gases issuing from the converter. The gases then pass through a mass of material containing finely-divided platinum. This may be platinised asbestos (§ 1228) or some other substance (*e.g.*, anhydrous magnesium sulphate) coated with platinum. Here the reaction to sulphur trioxide occurs, producing heat, and the gases, containing mainly nitrogen and sulphur trioxide, pass out, a part going through the heat exchanger and heating up the entering gases. The sulphur trioxide on cooling forms a mist of fine particles, and these are difficult to absorb in water; consequently the use of 98 per cent. sulphuric acid as an absorbing agent is preferred. The acid flows down towers packed with quartz, up which passes the gas containing the sulphur trioxide mist. The solution of sulphur trioxide in sulphuric acid, known as 'oleum,' is in great request in the synthetic dye and drug industry, and some half-million tons of it are sold as such. If it is required to produce ordinary sulphuric acid, water is added, with due precautions, to the oleum,

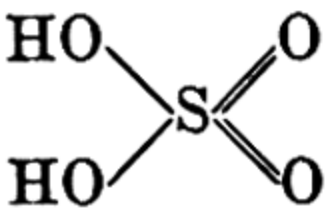
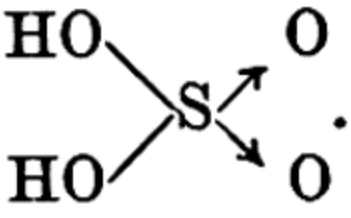
$$SO_3 + H_2O = H_2SO_4.$$

*Very pure sulphuric acid* may be made by cooling the concentrated acid. Crystals of pure sulphuric acid, melting at 10° C. if quite pure, separate out and may be drained from the mother liquor and allowed to melt.

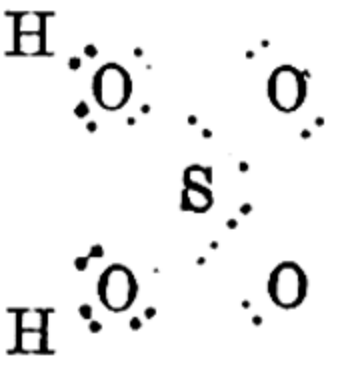
**931. Formula of Sulphuric Acid.**—The formation of sulphuric acid from sulphur trioxide and water shows its formula to be $H_2SO_4$. Its structural formula is demonstrated by the following facts. It contains two hydroxyl groups, for phosphorus pentachloride (*q.v.*) converts it first into chlorsulphonic acid, $HO.SO_2Cl$, and then into sulphuryl chloride, $SO_2Cl_2$. Since only one chlorsulphonic acid is known the two hydroxyl groups are probably symmetrically situated with respect to the remainder of the molecule.

Its formula is therefore $SO_2(OH)_2$.

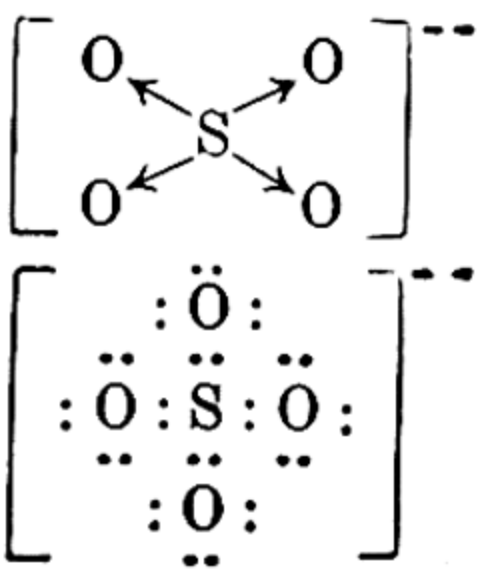
The structure of the $=SO_2$ grouping may be  , or possibly  (*v. infra*). The formula  is unlikely as representing an unstable peroxide-like grouping. The formula for undissociated sulphuric acid is then

 or  .

The arrangement of the electrons is then




The sulphate ion $SO_4^{--}$ probably has the structure




The double negative charge is occasioned by the fact that two electrons have been taken in from the basic radical of the acid or salt. One sulphur and four oxygen atoms have 30 valency electrons ; the above formula shows 32.

**932. Properties.**—Sulphuric acid is a colourless liquid of oily consistency. It is odourless, though when heated it gives off choking fumes of sulphur trioxide and sulphuric acid vapour. In *very* dilute solution it has the pleasant sour taste common to acids.

It has little or no physiological action when dilute. The concentrated acid is, however, intensely corrosive to all the tissues of the body. If swallowed it destroys the mouth, throat and stomach, and quickly causes death. It causes very serious burns if let fall on the skin. In case of such an accident the place should be instantly *flooded* with water—a little water is worse than none—and afterwards dusted with bicarbonate of soda, chalk or some other *mild* alkali.

Sulphuric acid, when pure, has a density of 1·84. When diluted there is a considerable contraction in volume so that the 94 per cent. acid is as dense as the pure acid.

Sulphuric acid freezes at about 10·5° C. when quite pure. The laboratory acid contains usually 2 per cent. of water and freezes at a much lower temperature—usually below 0° C. It boils about 290° C. with decomposition, in consequence of which the boiling point finally rises to 337° C.

Pure sulphuric acid does not conduct electricity, for it is not dissociated, but the addition of a very little water renders it conducting.

Sulphuric acid readily dissolves sulphur trioxide, forming solutions known as fuming sulphuric acid, Nordhausen sulphuric acid or oleum. These have the properties of the concentrated acid in an accentuated degree.

**933. Chemical Properties.**—Sulphuric acid decomposes when heated above 290° C., forming sulphur trioxide and water. These recombine on cooling: $H_2SO_4 \rightleftharpoons H_2O + SO_3$. At very high temperatures water, sulphur dioxide and oxygen are formed.

The remaining properties of sulphuric acid fall under three headings :.—

(1) The action of sulphuric acid on water and on compounds which can furnish it by their decomposition.

(2) The acidic properties of sulphuric acid.

(3) The oxidising action of sulphuric acid.

**934. Sulphuric Acid and Water.**—The behaviour of sulphuric acid towards water is interesting. When the two substances are mixed, a rise in temperature is at once noticed, and the mixture may reach a temperature of 120° C. This phenomenon may cause dangerous accidents, for if either the acid or the water when mixed are already hot, a violent ebullition of steam may eject the hot acid from the vessel on to anyone standing near. Even if the acid and water are both cold, this may occur if the error is made of pouring the water into the acid, for the rapid heating of the small quantity of water at first added may raise its temperature to the boiling point. If, however, the acid is poured in a thin stream into the well-stirred water no accident can occur, for the relatively large mass of water absorbs the heat formed, and by the time that much acid has been added the boiling point of the mixture will exceed any temperature reached. Always therefore pour the *acid* into the *water*. These considerable heat changes on dilution suggest chemical action; but there has been doubt as to whether any compound of acid and water is formed. In favour of the existence of such a compound there is the following evidence :—

(1) The heat evolved in the mixing is hard to account for on any other theory.

(2) Crystals of the hydrates $H_2O.H_2SO_4$ and $2H_2O.H_2SO_4$ have been isolated and also a hydrate $H_2SO_4.4H_2O$.

(3) Curves representing the variation of the melting points, specific gravity and vapour pressure of dilute sulphuric acid with composition give changes of inflexion at one or more points corresponding to the compositions represented by these hydrates.

These hydrates are not stable compounds, for on heating dilute sulphuric acid water is given off until a composition of 98 per cent.

$H_2SO_4$ is reached, when further heating merely causes this constant boiling mixture to distil over (cf. HCl, § 1055).

This action of sulphuric acid upon water makes it useful as a drying agent for such gases and liquids as it does not attack. The drying is not complete, for the acid has a minute vapour pressure which is further increased as soon as the acid has become at all diluted. However, where *intensive* drying (§ 205) is not required sulphuric acid is the most convenient drying agent.

Sulphuric acid reacts with numerous substances which can break up in such a way as to yield water, and combines with the water so obtained. Thus, from formic acid carbon monoxide is produced.

$$CH_2O_2 + H_2SO_4 = CO + (H_2SO_4 + H_2O).$$

Other examples are the production of ethylene from alcohol (§ 543), the decomposition of oxalic acid (§ 554).

Many organic substances are charred by concentrated sulphuric acid, *i.e.*, converted into carbon, water and various oxidation products. Thus sugar, starch, and the fibres of cotton and wool are all converted into a black amorphous mass. The destructive effect of the acid upon the skin, clothes, etc., is due to this cause.

**935. Acidic Properties of Sulphuric Acid.**—Dilute sulphuric acid exhibits the typical properties of a strong acid (§ 161 *seq.*). It reddens litmus, conducts electricity, forms sulphates and hydrogen with most metals, converts basic oxides and hydroxides into sulphates, etc.

In the true sense sulphuric acid is not one of the strongest acids, for it is not completely dissociated even in fairly dilute solution. Sulphuric acid is, on the other hand, stronger than any acid except the hydrogen halides, perchloric acid and nitric acid. The Raman spectra of its solution show that the $HSO_4^-$ ion is present in fairly strong solutions (*c.* 50 per cent.), but that at greater dilutions the $SO_4^{--}$ ion predominates.

Dilute sulphuric acid reacts with all the metals[1] except antimony, bismuth, mercury, copper, lead and the noble metals, forming hydrogen and the sulphate of the metal,

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Concentrated sulphuric acid does not however react with the metals at all in the cold, and when heated yields sulphur dioxide and other products (*v. infra*).

**936. Oxidising Action of Sulphuric Acid.**—Dilute sulphuric acid has no oxidising action, but the concentrated acid, especially when hot, tends to oxidise substances according to the general equation,

$$H_2SO_4 + X = H_2O + SO_2 + XO.$$

[1] A resistant oxide film protects aluminium, chromium and nickel.

Occasionally the acid is further reduced to sulphur or hydrogen sulphide.

Thus sulphuric acid oxidises certain non-metals, *e.g.*, sulphur and carbon, to their oxides,

$$2H_2SO_4 + C = CO_2 + 2SO_2 + 2H_2O$$
$$2H_2SO_4 + S = 3SO_2 + 2H_2O.$$

Its action on the metals is of interest. The main products are the sulphate of the metal, sulphur dioxide, and water. It is probable that these are formed as a result of the oxidation of the metal and the reaction of the oxide with the acid,

$$\begin{aligned} Cu + H_2SO_4 &= (CuO) + H_2O + SO_2 \\ (CuO) + H_2SO_4 &= CuSO_4 + H_2O \\ \hline Cu + 2H_2SO_4 &= CuSO_4 + 2H_2O + SO_2. \end{aligned}$$

The theory is also advanced that the metal first forms sulphate and the hydrogen which then reacts with the acid.

$$\begin{aligned} Cu + H_2SO_4 &= CuSO_4 + (2H) \\ (2H) + H_2SO_4 &= 2H_2O + SO_2 \\ \hline Cu + 2H_2SO_4 &= CuSO_4 + 2H_2O + SO_2. \end{aligned}$$

This theory is less probable, in view of the fact that metals which are not known to yield hydrogen with acids under any circumstances —silver, mercury—are attacked by concentrated sulphuric acid with little less vigour than the metals which do yield hydrogen (but see § 278).

The reaction of metals with sulphuric acid may yield other by-products.

Copper at lower temperatures (130–170° C.) in addition to the sulphate, forms some cuprous sulphide, the main reaction being

$$\begin{aligned} 5Cu + H_2SO_4 &= H_2O + Cu_2S + 3(CuO) \\ 3(CuO) + 3H_2SO_4 &= 3H_2O + 3CuSO_4 \\ \hline 5Cu + 4H_2SO_4 &= 4H_2O + Cu_2S + 3CuSO_4. \end{aligned}$$

Above 270° C. the formation of cuprous sulphide no longer occurs and anhydrous copper sulphate, sulphur dioxide and water are the only products.

Zinc, particularly if the acid contains a few parts of water per cent. forms sulphur, as well as sulphur dioxide.

$$3Zn + 4H_2SO_4 = 3ZnSO_4 + 4H_2O + S.$$

Still more dilute acid produces hydrogen sulphide together with hydrogen. We may write the equation,

$$4Zn + 5H_2SO_4 = 4ZnSO_4 + 4H_2O + H_2S.$$

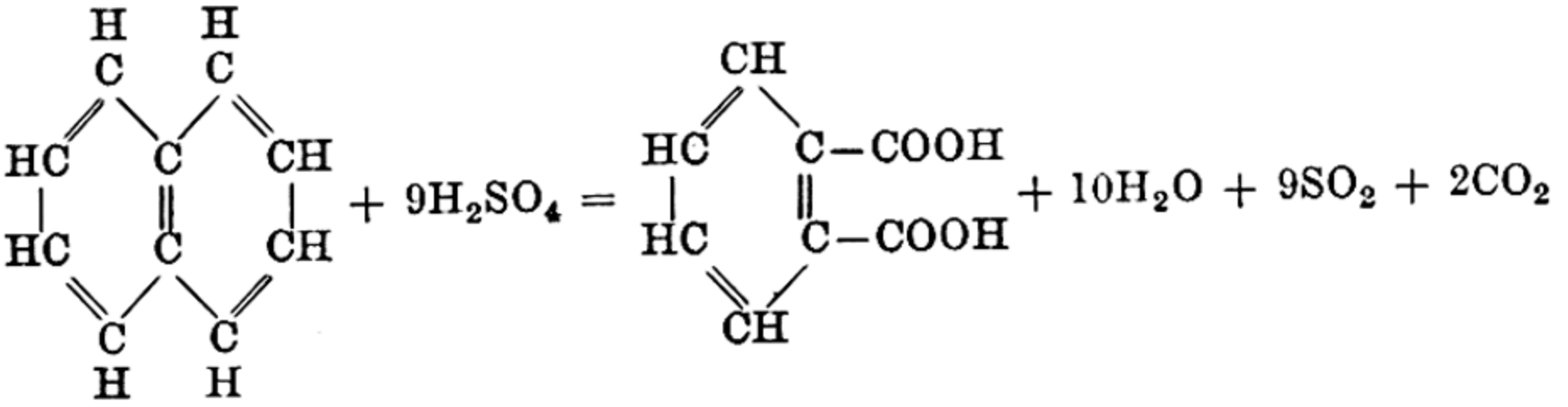
The oxidising effect of sulphuric acid is noticeable in its reactions with bromides and iodides. Sulphuric acid oxidises a part of the hydrogen bromide formed by the first reaction to bromine,

$$H_2SO_4 + KBr = KHSO_4 + HBr$$
$$2HBr + H_2SO_4 = 2H_2O + Br_2 + SO_2.$$

Iodides actually reduce the acid to sulphur and hydrogen sulphide.

$$H_2SO_4 + KI = KHSO_4 + HI$$
$$6HI + H_2SO_4 = 4H_2O + S + 3I_2$$
$$8HI + H_2SO_4 = 4H_2O + H_2S + 4I_2.$$

The oxidation of a compound by sulphuric acid is used commercially in the preparation of phthalic acid $C_8H_6O_4$, from naphthalene $C_{10}H_8$.




Mercuric sulphate acts as a catalyst.

**937. Detection and Estimation of Sulphates and Sulphuric Acid.**—The usual method is to bring the substance into solution, acidify with dilute hydrochloric acid, and add barium chloride solution. A white precipitate indicates the presence of a sulphate or sulphuric acid,

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

The presence of an acid is essential, for many barium salts are insoluble in water, but only the sulphate and silicofluoride are insoluble in hydrochloric acid. A confirmatory test consists in heating the substances on charcoal with sodium carbonate in the reducing blowpipe flame. If a sulphate is present, a sulphide is formed and the resultant mass will, when taken up in a little water, give a black precipitate with lead acetate, or discolour a silver coin.

**938. The Sulphates.**—There are three classes of sulphates, acid sulphates or bisulphates, normal sulphates and basic sulphates.

The only *acid sulphates* of importance are those of the alkali metals, $KHSO_4$, $NaHSO_4$. They are crystalline salts and behave in solution like mixtures of sulphuric acid and the normal salt.

Heated alone to redness they decompose, yielding the normal sulphate and sulphuric acid,

$$2NaHSO_4 = Na_2SO_4 + H_2SO_4.$$

They are further discussed under the heading of the metals in question.

*Normal Sulphates.*—Most of these normal sulphates are freely soluble salts, well crystallised usually with water of crystallisation. Exceptions are lead and barium and strontium sulphates, which are practically insoluble, calcium and silver sulphates, which are sparingly soluble. Many bivalent sulphates crystallise well with water of crystallisation, and were known as vitriols, Lat. *vitriolum*, 'a piece of glass,' from the fact that they were among the first transparent crystals known. Thus we have :—

| | | |
|---|---|---|
| Copper sulphate | $CuSO_4.5H_2O$ | . Blue vitriol. |
| Ferrous sulphate | $FeSO_4.7H_2O$ | . Green vitriol. |
| Zinc sulphate | $ZnSO_4.7H_2O$ | . White vitriol. |

The sulphates readily form double salts, of which two classes are particularly notable.

The first of these is the alums (§ 493).

The name alum is given to the double salt composed of the sulphates of a tervalent metal and the sulphate of a univalent metal, crystallising with twenty-four molecules of water.

$$M_2'SO_4.M_2'''(SO_4)_3.24H_2O$$

or

$$M'[M'''(SO_4)_2].12H_2O.$$

The name is taken from potassium aluminium sulphate, the first known alum, but there is no need for there to be any aluminium in an alum. They crystallise very well in octahedral crystals.

Common examples are :—

| | |
|---|---|
| Potash alum . . | $K_2SO_4.Al_2(SO_4)_3.24H_2O$ |
| Ammonium alum . | $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$ |
| Chrome alum . . | $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ |
| Iron ammonium alum. | $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$ |

Another set of double sulphates, the so-called false alums, consist of the sulphate of a monovalent metal, the sulphate of a divalent metal and six molecules of water of crystallisation. These may be represented as

$$M'_2[M''(SO_4)_2].6H_2O$$

or

$$M'_2SO_4.M''SO_4.6H_2O.$$

| | |
|---|---|
| Ferrous ammonium sulphate . | $FeSO_4.(NH_4)_2SO_4.6H_2O$ |
| Cupric potassium sulphate . | $CuSO_4.K_2SO_4.6H_2O$ |

The normal sulphates are of varying stability to heat. Those of the alkali metals and alkaline earth metals are stable. Those of the heavy metals are decomposed when heated, first into basic salts, then into the oxides and sulphur trioxide,

$$CuSO_4 = CuO + SO_3.$$

Ferrous sulphate is exceptional in forming also sulphur dioxide (§ 1160). When heated with carbon they are reduced, usually to the sulphide,

$$BaSO_4 + 4C = BaS + 4CO.$$

**939. Pyrosulphuric Acid $H_2S_2O_7$** is prepared by the action of sulphur trioxide on sulphuric acid and is contained in fuming sulphuric acid. The acid crystallises as a solid, melting at 35° C.

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

Definite salts, the *pyrosulphates*, are formed, so the acid is probably not merely a loose compound, $H_2SO_4.SO_3$.

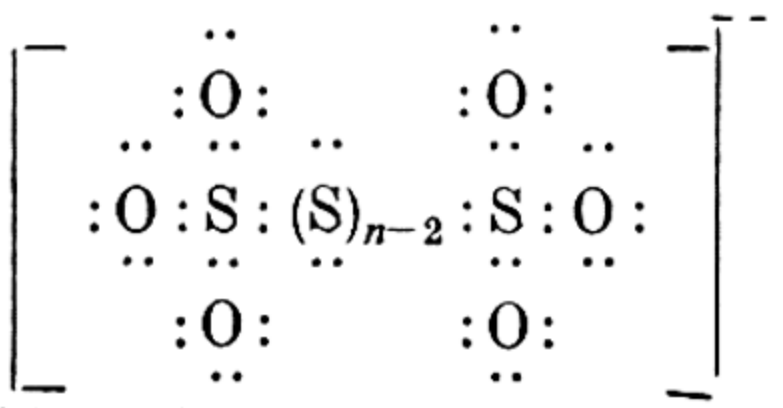
**940. The Polythionic Acids.**—The five acids of this series are of little practical importance. They have the general formula

$$H_2S_nO_6,$$

and the structure

$$S_{n-2}\begin{cases} SO_2.OH \\ SO_2.OH. \end{cases}$$

The electronic structure of their ions appears to be



**941. Dithionic Acid $H_2S_2O_6$** is prepared by the action of sulphur dioxide on a suspension of ferric hydroxide at 0° C.

$$2Fe(OH)_3 + 3H_2SO_3 = Fe_2(SO_3)_3 + 6H_2O$$
$$Fe_2(SO_3)_3 = FeS_2O_6 + FeSO_3.$$

The addition of barium hydroxide to the mixture of ferrous dithionate and sulphite forms a precipitate of barium sulphite and ferrous hydroxide and leaves barium dithionate in solution. The latter is treated with the exact quantity of sulphuric acid necessary to precipitate the barium filtered and evaporated *in vacuo*.

$$BaS_2O_6 + H_2SO_4 = BaSO_4 + H_2S_2O_6.$$

The acid when warmed decomposes into sulphur dioxide and sulphuric acid,

$$H_2S_2O_6 = H_2SO_4 + SO_2.$$

In the air it oxidises to sulphuric acid,

$$2H_2S_2O_6 + 2H_2O + O_2 = 4H_2SO_4.$$

The dithionates, when heated in solution or otherwise, form sulphates and sulphur dioxide,

$$Na_2S_2O_6 = Na_2SO_4 + SO_2.$$

**942. Trithionic Acid.**—Potassium trithionate is prepared by the action of sulphur on potassium bisulphite

$$6KHSO_3 + 2S = 2K_2S_3O_6 + K_2S_2O_3 + 3H_2O.$$

The trithionates are also prepared by the action of persulphates on thiosulphates,

$$K_2S_2O_8 + 2K_2S_2O_3 = 2K_2SO_4 + K_2S_4O_6.$$

The free acid is obtained by the action of hydrofluosilicic acid on the potassium salt, insoluble potassium fluosilicate being precipituted,

$$K_2S_3O_6 + H_2SiF_6 \rightleftharpoons H_2S_3O_6 + K_2SiF_6\downarrow.$$

The acid readily decomposes to sulphur, sulphur dioxide and sulphuric acid,

$$H_2S_3O_6 = H_2SO_4 + SO_2 + S.$$

The trithionates are mild reducing agents, oxidised by air to sulphates, sulphur and sulphur dioxide, and the same products are formed when they are heated.

**943. Tetrathionic Acid $H_2S_4O_6$.**—The tetrathionates are prepared by the action of iodine on the thiosulphates (§ 924),

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

Lead thiosulphate is best used,

$$2PbS_2O_3 + I_2 = PbI_2\downarrow + PbS_4O_6.$$

The insoluble lead iodide is filtered off and the lead tetrathionate treated with sulphuric acid,

$$PbS_4O_6 + H_2SO_4 = PbSO_4\downarrow + H_2S_4O_6.$$

The acid is filtered off from the insoluble lead sulphate.

Tetrathionic acid is a strong acid, known only in solution. It decomposes when concentrated,

$$H_2S_4O_6 = H_2SO_4 + SO_2 + 2S.$$

The tetrathionates decompose similarly.

**944. Pentathionic Acid $H_2S_5O_6$** is formed when hydrogen sulphide is slowly passed into a nearly saturated solution of sulphurous acid. Much sulphur and also other thionic acids are formed,

$$5H_2S + 10SO_2 = 3H_2S_5O_6 + 2H_2O.$$

It is freed from sulphuric acid by the addition of barium carbonate and is purified by filtration from sulphur. The filtrate is concentrated *in vacuo*.

The acid and its salts all decompose on heating into sulphuric acid or sulphates, sulphur dioxide and sulphur,

$$H_2S_5O_6 = H_2SO_4 + SO_2 + 3S.$$

**945. Hexathionic Acid $H_2S_6O_6$** appears to exist in the solutions described above as obtained from hydrogen sulphide and sulphurous acid.

**946. Persulphuric Acid $H_2S_2O_8$.**—When sulphuric acid is electrolysed only hydrogen and oxygen normally result. If, however, the solution electrolysed is ice-cold and of strength about 50 per cent., and if the electrolysis is conducted with a high current density (500 amps. per sq. dm. of anode) persulphuric acid results.

The bisulphate ions $HSO_4^-$ are discharged at the anode and unite, forming $H_2S_2O_8$,

$$2HSO_4 = H_2S_2O_8.$$

The acid soon decomposes, forming Caro's acid, which decomposes to sulphuric acid and hydrogen peroxide,

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4$$
$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2.$$

*The persulphates* are valuable oxidising agents. Potassium persulphate may be prepared by electrolysis of a solution of potassium bisulphate in a cell divided by a porous partition. The solution must be cold and the current density high,

$$SO_4^{--} = SO_4 + 2\ominus$$
$$K_2SO_4 + SO_4 = K_2S_2O_8.$$

The potassium salt, being sparingly soluble, crystallises out.

The persulphates are powerful oxidising agents. When heated in solution they form sulphates and oxygen.

$$2K_2S_2O_8 + 2H_2O = 2K_2SO_4 + 2H_2SO_4 + O_2.$$

Heated alone they give off sulphur trioxide and oxygen. They readily oxidise most substances capable of oxidation. Ferrous salts are oxidised to ferric,

$$2FeSO_4 + K_2S_2O_8 = K_2SO_4 + Fe_2(SO_4)_3,$$

manganous salts to manganese dioxide, chromium salts to chromates. Iodine is liberated from iodides. Their solutions dissolve many metals,

$$K_2S_2O_8 + Zn = K_2SO_4 + ZnSO_4.$$

They are powerful bleaching agents, but are not used commercially on account of their destructive action upon the fibre of cloth, paper, etc.

When treated with sulphuric acid, oxygen, together with some ozone, is liberated.

**947. Monopersulphuric Acid, Caro's Acid $H_2SO_5$,** is prepared by the action of sulphuric acid on potassium persulphate in the cold,

$$H_2SO_4 + K_2S_2O_8 = H_2SO_5 + K_2SO_4 + SO_3.$$

It is better prepared by the action of 100 per cent. hydrogen peroxide on chlorsulphonic acid (*q.v.*),

$$HO.OH + Cl.SO_2OH = HO.O.SO_2.OH + HCl.$$

Monopersulphuric acid is a crystalline solid. It readily decomposes in solution to hydrogen peroxide and sulphuric acid,

$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2.$$

It is a very powerful oxidising agent.

No monopersulphates are known.

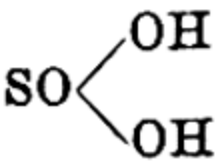
**948. Acid Halides of Sulphur.**—There is a series of acid halides of sulphur derived, as will be seen, from oxyacids of sulphur, by replacement of their hydroxyl groups by chlorine or other halogen atoms. The chief halides of this type are the thionyl and sulphuryl compounds.

**949. The Thionyl Halides.**—These include :

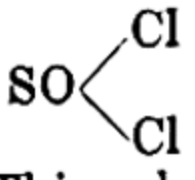
| | |
|---|---|
| Thionyl fluoride . . . . . | $SOF_2$ |
| Thionyl chloride . . . . . | $SOCl_2$ |
| Thionyl bromide . . . . . | $SOBr_2$ |

The only one of these of any importance is thionyl chloride.

This substance is the *acid chloride* of sulphurous acid,



Sulphurous acid.



Thionyl chloride.

It is made by the action of phosphorus pentachloride on sulphur dioxide,

$$SO_2 + PCl_5 = SOCl_2 + POCl_3.$$

or by the action of sulphur trioxide on sulphur monochloride, which method is used on the commercial scale,

$$SO_3 + S_2Cl_2 = SOCl_2 + SO_2 + S.$$

It is a colourless liquid which emits pungent acid fumes ; it boils at 78° C.

Thionyl chloride reacts with water, giving sulphurous acid and hydrochloric acid,

$$SOCl_2 + 2H_2O = H_2SO_3 + 2HCl.$$

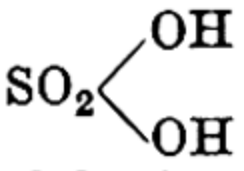
It finds a use in organic chemistry as a means of replacing the hydroxyl group by chlorine,

$$X - OH + SOCl_2 = HCl + SO_2 + X - Cl.$$

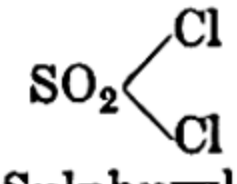
The reaction of thionyl fluoride and bromide are similar in character.

**950. The Sulphuryl Halides.**—Sulphuryl fluoride $SO_2F_2$, Sulphuryl chloride $SO_2Cl_2$.

These may be regarded as the acid halides of sulphuric acid,



Sulphuric acid.



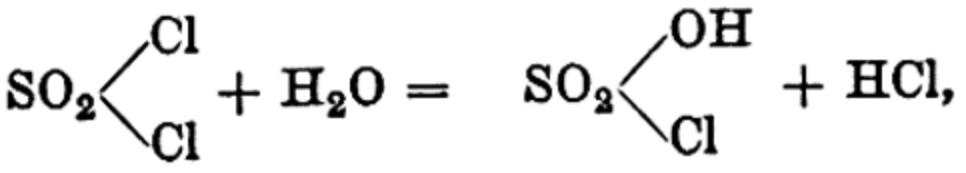
Sulphuryl chloride.

Sulphuryl chloride is made by the direct action of chlorine on excess of sulphur dioxide in presence of activated charcoal,

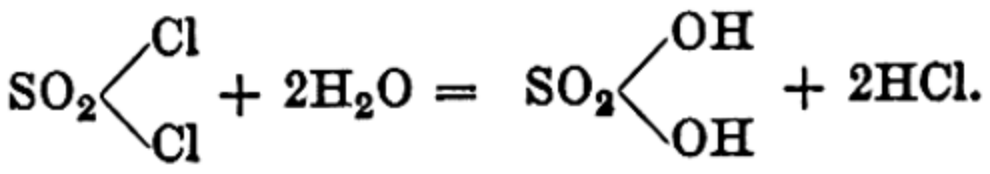
$$SO_2 + Cl_2 = SO_2Cl_2.$$

If the reaction vessel is kept cold by surrounding it with ice or running water the sulphuryl chloride condenses.

Sulphuryl chloride is a colourless liquid of B.P. 69° C. With a little water it forms first chlorsulphonic acid,



then with more water, sulphuric acid,



Like thionyl chloride, it is used technically for making the acid chlorides of organic acids, being cheaper than phosphorus pentachloride, which is used for this purpose in the laboratory,

$$2CH_3COONa + SO_2Cl_2 = Na_2SO_4 + 2CH_3.CO.Cl.$$

Sodium acetate. Acetyl chloride.

*Sulphuryl fluoride* is prepared by a similar method. It is a gas which reacts with water to form sulphuric and hydrofluoric acid.

**951. Pyrosulphuryl Chloride $S_2O_5Cl_2$** may be made by the action of fuming sulphuric acid on carbon tetrachloride,

$$2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2.$$

It is a liquid boiling at 153° C. It is decomposed by water, first to chlorsulphonic acid, then to hydrochloric and sulphuric acids,

$$S_2O_5Cl_2 + 2H_2O = SO_2\begin{<}OH\\Cl\end{>} + H_2SO_4 + HCl.$$

**952. Chlorsulphonic Acid $SO_2\begin{<}Cl\\OH\end{>}$** is made by passing well dried hydrogen chloride into fuming sulphuric acid until no more gas is absorbed. The acid is then distilled in a current of dry HCl, and the portion boiling between 145°–160° C. is condensed

$$HCl + SO_3 = HO.SO_2.Cl.$$

It is a colourless liquid which fumes in air. It boils at 151° C. and its vapour decomposes according to the equation

$$2Cl.SO_2OH = Cl_2 + SO_2 + H_2O + SO_3.$$

Water reacts violently with it, forming hydrochloric and sulphuric acids,

$$Cl.SO_2.OH + H_2O = HCl + H_2SO_4.$$

## Sulphur Halides

The halides of sulphur include :—

| | |
|---|---|
| Sulphur hexafluoride . . . . . | $SF_6$ |
| Sulphur decafluoride . . . . . | $S_2F_{10}$ |
| Sulphur monochloride . . . . . | $S_2Cl_2$ |
| Sulphur dichloride . . . . . | $S_2Cl_4$ |
| Sulphur tetrachloride . . . . . | $SCl_4$ |
| Sulphur monobromide . . . . . | $S_2Br_2$ |

There are no compounds of iodine and sulphur.

**953. Sulphur Hexafluoride $SF_6$** is made by the direct action of fluorine upon sulphur. It is interesting in several ways. It is a gas, colourless and without smell. The chief points of interest about it are, firstly, that its formula demonstrates the sexivalency of sulphur very clearly and, secondly, that it is very inert chemically, not being attacked by water as are the other halides of sulphur. In this respect it resembles carbon tetrachloride and differs from all other non-metallic halides. The explanation of its remarkable inertness is the same as that given for the inertness of carbon tetrachloride, namely that the sulphur is exerting its full co-ordinate valency as well as covalency, and so cannot attach itself to the molecule of any other substance.

By fractionating liquid sulphur hexafluoride, the very stable decafluoride has been made. Lower fluorides, $SF_4$, etc., probably exist.

**954. Sulphur Monochloride $S_2Cl_2$** may be made by the same method as is described for the making of phosphorus trichloride (p. 573). Sulphur is placed in the retort (Fig. 150) and is maintained in the melted condition by gentle heating, using a sand-bath.

On the commercial scale it is obtained as a by-product in the manufacture of carbon tetrachloride from carbon disulphide,

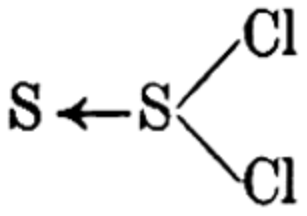
$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2.$$

Sulphur monochloride is a yellow liquid with a peculiar unpleasant and irritating smell. It fumes in moist air. It boils at 138° C.

Sulphur monochloride is decomposed slowly by water; thiosulphuric acid, sulphurous acid, sulphur, hydrogen sulphide, various thionic acids, and hydrogen chloride being formed.

Sulphur monochloride readily dissolves sulphur. Its chief use is in vulcanising india-rubber, which is exposed to its vapour in a closed chamber or immersed in a solution of the chloride in benzene.

It is probably a mixture of the forms




and $Cl-S-S-Cl$.

**955. Sulphur Dichloride $SCl_2$.**—This substance is produced by saturating sulphur monochloride with chlorine,

$$S_2Cl_2 + Cl_2 = 2SCl_2.$$

It is a dark red liquid which decomposes on heating into the monochloride and chlorine.

**956. Sulphur Tetrachloride $SCl_4$** is prepared by the prolonged action of chlorine on sulphur monochloride at − 20°C. Its formula is considered to be

$$[SCl_3]^+Cl^-$$

It is an unstable substance, decomposing even at room temperature.

With water hydrochloric and sulphurous acids are formed,

$$SCl_4 + 3H_2O = H_2SO_3 + 4HCl.$$

**957. Sulphur Monobromide $S_2Br_2$** is a red liquid obtained by dissolving sulphur in bromine. Its reactions are similar to those of sulphur monochloride.

No iodides of sulphur are known.

## SELENIUM Se, 78·96

The element selenium shows a considerable resemblance to sulphur, bearing to the latter element much the same relationship as that of arsenic to phosphorus.

Thus the acids derived from selenium are weaker and less stable than the corresponding acids derived from sulphur; hydrogen selenide is less stable than hydrogen sulphide.

**958. Occurrence.**—Selenium is widely distributed in Nature in small quantities, chiefly as metallic selenides. It is chiefly recovered from the anode slimes of the electrolytic refining of copper, nickel, and lead, and also to some extent from a deposit produced in the lead chambers of sulphuric acid plant.

The crude deposits are taken up in a mixture of sulphuric acid and potassium nitrate which oxidises the selenium to selenious acid. Neutralisation with sodium carbonate precipitates other metals (copper, lead, etc.) as their carbonates, and the remaining selenites are reduced to selenium with sulphur dioxide.

Selenium, like sulphur, exists in several allotropic forms. One of these, which is crystalline in character, increases greatly in electrical conductivity when exposed to light, a property utilised in numerous types of electrical and optical apparatus.

**959. Chemical Properties.**—Selenium burns with a purple flame, forming selenium dioxide $SeO_2$. Heated in hydrogen it forms some hydrogen selenide,

$$Se + H_2 \rightleftharpoons H_2Se.$$

It reacts with fluorine, forming $SeF_4$ and $SeF_6$, and with chlorine, forming chlorides, $Se_2Cl_2$ and $SeCl_4$. Sulphur and selenium appear to form only mixtures and no compounds.

Nitric acid oxidises selenium to selenious acid $H_2SeO_3$.

**960. Atomic Weight of Selenium.**—From the vapour density of its volatile compounds and the conversion of silver selenite $Ag_2SeO_3$ into silver chloride, the value 79·2 has been adopted.

**961. Selenium Hydride, Seleniuretted Hydrogen $SeH_2$,** is best made by the action of dilute hydrochloric acid on ferrous selenide,

$$FeSe + 2HCl = FeCl_2 + SeH_2.$$

It is a colourless gas of very unpleasant odour. It is a good deal more poisonous and fetid than hydrogen sulphide. It is soluble in water.

It is readily decomposed when heated. If passed through a hot glass tube crystalline selenium is deposited, $H_2Se = Se + H_2$, on the cooler part of the tube. Selenium hydride burns, forming water and selenium dioxide. Solutions of hydrogen selenide are easily oxidised in a similar manner to those of hydrogen sulphide,

$$2SeH_2 + O_2 = 2Se + 2H_2O.$$

It acts on solutions of metallic salts in much the same way as hydrogen sulphide. The *selenides* are formed by the action of hydrogen selenide on metallic salts or by the action of selenium on the metal itself.

On the whole the selenides resemble the sulphides.

**962. Selenium Dioxide** is prepared by evaporating a solution of selenious acid prepared by oxidising selenium with nitric acid,

$$H_2SeO_3 = H_2O + SeO_2.$$

It is also prepared by heating the element in dry oxygen.

Selenium dioxide is a white crystalline solid which sublimes at *c.* 300° C. It dissolves in hot water, forming selenious acid.

Selenium does not appear to form a trioxide analogous to sulphur trioxide. Its existence has been reported but does not seem to have been confirmed.

Selenium dioxide is finding a rapidly increasing use as an oxidising agent in organic work. The reaction is $SeO_2 + 2X = Se + 2XO$.

**963. Selenious Acid $H_2SeO_3$** is prepared by the oxidation of selenium by nitric acid,

$$Se + 4HNO_3 = H_2SeO_3 + H_2O + 4NO_2.$$

It crystallises in colourless prisms. It differs from sulphurous acid in that it is readily reduced to the element by organic compounds, sulphur dioxide, etc. Selenious acid can also be oxidised by chlorine or bromine to selenic acid. The *selenites* are very poisonous salts.

**964. Selenic Acid $H_2SeO_4$.**—The acid is prepared by oxidising selenious acid.

$$H_2SeO_3 + Cl_2 + H_2O = H_2SeO_4 + 2HCl.$$

The solution may be evaporated *in vacuo*, and then solidifies as a colourless crystalline solid. Selenic acid resembles sulphuric in its vigorous action on water and its consequent corrosive action on organic matter. The dilute acid is remarkable in that it attacks gold and copper as well as other metals, forming *selenates*.

Selenic acid differs from sulphuric in the ease with which it is decomposed by heat below its boiling point,

$$2H_2SeO_4 = 2H_2O + 2SeO_2 + O_2,$$

and in its ready reduction to selenious acid or even selenium.

The *selenates* are isomorphous with the sulphates, which they much resemble.

## TELLURIUM Te, 127·61

**965. Occurrence.**—The element tellurium is fairly widely distributed, but usually in small quantity. It occurs as tellurides, such as bismuth tellurides $Bi_2Te_3$, *tetradymite*, which is the commonest of these ores.

**966. Extraction.**—Tellurium, like selenium, is obtained chiefly from the anode slimes of the electrolytic refinement of other metals. In the extraction of selenium, tellurium is precipitated as the oxide, together with the carbonates and hydroxides of other metals, when the solution of these anode slimes in sulphuric acid is neutralised. The tellurium oxide is extracted, as tellurite, from this mixed precipitate with caustic soda, and reprecipitated with acid. The purified oxide is then reduced to tellurium with carbon in a small furnace.

*Allotropy.*—Two forms of tellurium exist, a crystalline form and an amorphous form, prepared by precipitation. The latter form is unstable.

The presence of 0·1 per cent. of tellurium in lead enhances considerably its mechanical properties, and confers an added resistance to chemical corrosion.

**967. Properties.**—Crystalline tellurium has a definitely metallic appearance and lustre. It is very brittle. It melts at 452° C. and boils at a red heat.

Tellurium burns with a blue flame to tellurium dioxide. It is not attacked by ordinary acids but is oxidised by nitric and sulphuric acid to tellurium dioxide, etc. Chlorine converts the element into tellurium dichloride $TeCl_2$, and tellurium tetrachloride $TeCl_4$.

Tellurium and its compounds are somewhat poisonous. They produce in man a most unpleasing garlic-like odour of the breath and whole body. Chemists investigating certain compounds of tellurium have been almost excluded from society by the penetrating odour they exhale.

**968. Atomic Weight of Tellurium.**—Reference to the periodic table (pp. 154, 155) shows that if that table were to be drawn up in strict ascending order of atomic weight tellurium and iodine should change places, tellurium having an atomic weight of 127·5, while the figure for iodine is 126·93. Elabor-

ate investigations were carried out to search for some source of error, but the above figures are undoubtedly correct.

Tellurium has numerous volatile compounds; the gram-molecular weight of these never contains less than about 127·5 gms. of tellurium. This is accordingly the approximate atomic weight which is confirmed by Dulong and Petit's law.

The exact atomic weight has been determined in very many ways, such as (1) by converting $TeBr_4$ tellurium tetrabromide and $TeBr_2$ tellurium dibromide into silver bromide. Tellurium dioxide has been oxidised to the trioxide by permanganate and the ratio $TeO_2 : O$ thus determined, or reduced to tellurium and the rario $TeO_2 : Te$ determined. From about sixty different sets of experiments a probable value of about 127·61 emerges.

The work of Moseley and others showed that the place in the periodic table is given by the atomic number, *i.e.*, the difference between the number of protons and electrons in the nucleus. The atomic numbers do not necessarily, though exceptions are few, follow in the same order as the atomic weights. Tellurium consists actually of several *isotopes* of atomic weights, 126, 128, 130, and it is the preponderance of the second that gives it its anomalous atomic weight.

**969. Hydrogen Telluride $TeH_2$** may be prepared by the action of dilute acid upon zinc or magnesium telluride,

$$ZnTe + 2HCl = ZnCl_2 + TeH_2.$$

The gas may be separated from hydrogen by condensation in a freezing mixture.

It is a colourless foul-smelling gas which condenses to a liquid, boiling at 0° C. It is very unstable, and in other respects resembles hydrogen selenide.

**970. The Tellurides.**—Tellurium forms tellurides when melted with various metals. Some resemble the sulphides and selenides, while others, notably those of the heavy metals, rather resemble alloys.

**971. Tellurium Halides.**—These on the whole resemble the halides of sulphur. They are decomposed by water into halogen hydrides, tellurous acid, tellurium, etc. Certain double salts, such as $K_2TeBr_6$, can be prepared in a crystalline state, but tellerium cannot be regarded as forming the basic radical in any true salt.

**972. Tellurium Dioxide** is prepared by similar methods to selenium dioxide (§ 962). It differs from the latter in being almost insoluble in water. With alkalis it forms *tellurites*.

**973. Tellurium Trioxide $TeO_3$** is obtained by heating telluric acid to redness. It is acidic in character.

**974. Telluric Acid $H_2TeO_4.2H_2O$** is often written $H_2TeO_4$. It is, however, actually $H_6TeO_6$, *i.e.*, $Te(OH)_6$. (The ordinary tellurates are usually written $M_2TeO_4 . 2H_2O$, but there are also salts such as $Na_4TeO_5 . 8H_2O$. The first should be wirtten $M_2H_4TeO_6$ and the second $Na_4H_2TeO_6 . 7H_2O$.) It is prepared by dissolving tellurium in nitric acid and oxidising

$$Te + 4HNO_3 = H_2TeO_3 + H_2O + 4NO_2$$

the tellurous acid with chromic acid,

$$3H_2TeO_3 + 2H_2CrO_4 + 6HNO_3 + H_2O = 3H_6TeO_6 + 2Cr(NO_3)_3.$$

The acid $H_6TeO_6$ (formerly regarded as the dihydrate $H_2TeO_4 . 2H_2O$) crystallises out.

Telluric acid is a feeble acid, quite unlike sulphuric; it is readily reduced to tellurium by sulphur dioxide, etc.

**975. Survey of the Group VI. B.**—The group, oxygen, sulphur, selenium, tellurium, is one which illustrates well the gradation of properties usual in a group of the periodic table.

*The Elements.*—Oxygen, sulphur, selenium, tellurium, all show allotropy, but this is so common a phenomenon that it is not surprising. In physical properties the boiling points, melting points and densities rise with increasing atomic weight. The elements are all bivalent. Chemically, the reactivity of the elements in general diminishes with increasing atomic weight, and their compounds become less stable; the halides naturally being an exception to this rule, for compounds of halogens with non-metals are less stable than those with metalloids or metals.

*The Hydrides.*—Water behaves in a manner quite exceptional. The properties of the hydrides, those of water being excepted, vary regularly with increase of atomic weight. Thus water boils at 100° C., while hydrogen sulphide, selenide and telluride boil at — 61·8° C., — 42° C. and 0° C. respectively. Water is an associated liquid and may be regarded as made up of loose associations of two or three $H_2O$ molecules, and naturally it is not comparable with the non-associated hydrogen sulphide, etc. (The relation of hydrogen fluoride (B.P. 19° C.), to the other hydrogen halides (B.P. from — 83° C.) is instructively analogous.)

*The Oxides.*—The lower oxides of sulphur, selenium and tellurium are in each case acidic. As atomic weight increases, these oxides become more easily reduced and less easily oxidised. Thus sulphur dioxide is a reducing agent, while selenium dioxide is a useful oxidising agent. The higher oxide of tellurium, $TeO_3$, also is more easily reduced than sulphur trioxide.

The higher acids, sulphuric, selenic and telluric, show a rapid falling off in strength and also a decrease of stability as atomic weight increases.

# CHAPTER XXI

## CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM.

**976. Sub-Group VI. A.**—Group VI. A contains the important element chromium, and the somewhat rarer tungsten, molybdenum, and uranium. These elements resemble each other in that they have very variable valency. The highest valency in each case is six as shown in the trioxides and the fluorides, $MoF_6$, $WF_6$ and $UF_6$. They all form acidic trioxides, $CrO_3$, $MoO_3$, $WO_3$, $UO_3$, which form stable and important salts, the chromates, molybdates, tungstates and uranates.

### CHROMIUM Cr, 52·01

**977. Occurrence.**—The element chromium occurs chiefly as *chromite* or *chrome iron-ore*, which is ferrous chromite $FeCr_2O_4$ or $FeO.Cr_2O_3$, which in addition to being the source of chromium compounds, is a valuable refractory material for lining furnaces, etc. Lead chromate *crocoisite* $PbCrO_4$ also occurs native.

**978. Extraction.**—Chromium is prepared by two methods—

(1) Electrolysis of its salts.

(2) The aluminothermic method.

The preparation by electrolysis is much in use for the purpose of chromium plating. A coating of chromium upon metal gives it a pleasing bluish silvery tint and has the advantage of requiring little or no cleaning. It is possible to obtain a coherent coating only under certain conditions. The plating bath may consist of a hot solution (40° C.) of chromium trioxide (250 gms. per litre) and chromium sulphate (3–5 gms. per litre). A lead anode is employed with a current density of 11 amp. per sq. dm. of cathode.

The aluminothermic method may be applied in the laboratory by mixing well-dried chromium sesquioxide and aluminium powder in equivalent proportions in a large fire-clay crucible[1] embedded in a bucket full of sand. The mixture is fired by means of a piece of magnesium ribbon inserted in the mixture. The reaction evolves great heat and the melted chromium runs to the bottom of the crucible,

$$Cr_2O_3 + 2Al = Al_2O_3 + 2Cr.$$

[1] A small crucible does not become hot enough for the chromium to be melted.

The addition of some potassium dichromate improves the yield by raising the temperature of the reaction. The quantities, $Cr_2O_3$ 210 gms., $K_2Cr_2O_7$ 60 gms., *coarse* aluminium powder 96 gms., have been recommended.

Chromium is a bluish white metal. It is very hard, pure chromium being harder than glass, while chromium containing carbon is said to be only less hard than the diamond. It melts at a very high temperature, *c.* 1,920° C. The metal oxidises superficially when heated in air.

Chromium is acted on by dilute hydrochloric acid, though slowly,

$$2Cr + 6HCl = 2CrCl_3 + 3H_2.$$

Concentrated sulphuric acid attacks it, forming the sulphate and sulphur dioxide.

Concentrated nitric acid, however, renders the metal *passive*. This condition and its cause is discussed under Iron in § 1149.

The alloys of chromium and iron are of considerable importance. Chrome steels are made by heating chromite and anthracite in the electric furnace,

$$FeCr_2O_4 + 4C = Fe + 2Cr + 4CO.$$

The resulting 'ferro-chrome,' containing 40 to 80 per cent. of chromium, is then added to the requisite quantity of melted steel. Chrome steel, containing some 2 to 4 per cent. of carbon, is intensely hard and tough and is used in engineering work. An alloy of 84 per cent. iron, 13 per cent. chromium, and 1 per cent. nickel constitutes stainless steel, which is rapidly coming to the fore for numerous purposes. It does not rust and is at the same time of considerable strength. Chromium nickel alloys, which have a high melting point and are but little oxidised in air, are used for the windings of electric fires, etc.

**979. Atomic Weight of Chromium.**—From the densities of volatile chromium compounds, *e.g.*, $CrO_2Cl_2$, and from the evidence of Dulong and Petit's law, the atomic weight of chromium appears to be about 52. The chemical equivalent is about 17·3 in the chromium salts and half this value in the chromates. Its usual valencies are therefore 3 and 6.

The most accurate determination consisted of preparing pure silver chromate and dichromate. These were reduced by sulphur dioxide or otherwise and the silver was precipitated with all modern precautions as the chloride. The ratios $Ag_2CrO_4$ : 2AgCl and $Ag_2Cr_2O_7$ : 2AgCl yielded figures of 52·04 for the atomic weight. The accepted value is 52·01.

**980. Chromium Oxides.**—Chromium forms four oxides:

| | |
|---|---|
| Chromous oxide . . . . . | $CrO$ |
| Chromium sesquioxide . . . . | $Cr_2O_3$ |
| Chromium dioxide. . . . . | $CrO_2$ |
| Chromic anhydride . . . . | $CrO_3$ |

**981. Chromous Oxide CrO** is prepared by the oxidising action of dilute nitric acid on chromium amalgam. It cannot be made by heating *chromous hydroxide* prepared by the action of alkalis on chromous salts, as it decomposes into chromic oxide, hydrogen, and water.

**982. Chromic Oxide, Chromium Sesquioxide $Cr_2O_3$.**—Chromic oxide may be prepared by the action of heat on chromic hydroxide, obtained by the action of alkalis upon chromic salts,

$$CrCl_3 + 3KOH = Cr(OH)_3 + 3KCl$$
$$2Cr(OH)_3 = Cr_2O_3 + 3H_2O.$$

It may also be made by reducing the dichromate in various ways. Thus potassium dichromate may be heated with ammonium chloride,

$$K_2Cr_2O_7 + 2NH_4Cl \rightleftharpoons (NH_4)_2Cr_2O_7 + 2KCl$$
$$(NH_4)_2Cr_2O_7 \rightleftharpoons N_2 + 4H_2O + Cr_2O_3.$$

The green residue is washed free from potassium chloride and dried.

Chromium sesquioxide forms a powder of a green tint. It is often used as a pigment and is very permanent. Chromium sesquioxide is not decomposed by heating nor is it reduced by hydrogen. Carbon at a white heat, however, reduces it to the metal.

It is a basic oxide, but is only attacked very slowly by acids. When fused with alkalis it dissolves, perhaps to a chromite, and if air, or better, some oxidising agent such as potassium chlorate, is present this becomes oxidised to the yellow chromate,

$$Cr_2O_3 + 2KOH = 2KCrO_2 + H_2O$$
$$4KCrO_2 + 4KOH + 3O_2 = 4K_2CrO_4 + 2H_2O.$$

**983. Chromic Hydroxide $Cr(OH)_3$** is obtained as a gelatinous precipitate when caustic soda is added in theoretical amount to a solution of a chromium salt,

$$CrCl_3 + 3NaOH = Cr(OH)_3 + 3NaCl.$$

The green chromic salts (§ 997) give a green hydroxide : the violet salts give a grey-blue precipitate, which may be hydrated. The precipitate is filtered off, well washed, and dried. Chromic hydroxide decomposes when heated to form chromic oxide.

It dissolves readily in acids to form chromic salts and also to some extent in alkalis to a bluish solution. Chromites are probably not formed, for they cannot be isolated and the chromium will not diffuse through parchment. The solution is therefore probably colloidal chromic hydroxide. Chromic hydroxide in presence of alkalis is easily oxidised to chromate by bromine, hydrogen peroxide, etc.

$$2Cr(OH)_3 + 3Br_2 + 10NaOH = 2Na_2CrO_4 + 6NaBr + 8H_2O$$

**985. Chromium Dioxide $CrO_2$ (or $Cr_3O_6$)** has been regarded as chromic chromate $Cr_2O_3.CrO_3$. Organic compounds of chromium have now been discovered in which the element has a valency of four. It is possible then that the oxide is truly $CrO_2$, not $Cr_3O_6$. It is formed by heating chromium sesquioxide in air,

$$2Cr_2O_3 + O_2 \rightleftharpoons 4CrO_2.$$

It is also formed by the action of chromic acid on chromic hydroxide. It forms a black powder which decomposes at a red heat into the sesquioxide and oxygen. By the action of alkalis it is easily converted into chromium sesquioxide and a chromate.

**986. Chromium Trioxide, Chromic Anhydride $CrO_3$.**—Chromium trioxide is made by the action of sulphuric acid on potassium dichromate.

The simplest method is to add an excess of cold concentrated sulphuric acid to concentrated potassium dichromate solution, stirring well. On cooling, dark red crystals of the trioxide appear. The liquid is poured off and the excess of moisture removed by pressing on a porous plate. The crystals may be washed with concentrated nitric acid (sp. gr. 1·46), in which they are not soluble, pressed on a porous plate, and then gently dried on a sand-bath,

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2CrO_3.$$

Chromium trioxide forms deep red prismatic needles. It melts at 193° C. When heated further it forms brown chromic chromate and gives off oxygen at 250° C.,

$$6CrO_3 = 2Cr_3O_6 + 3O_2,$$

and on further heating yields chromium sesquioxide,

$$4CrO_3 = 2Cr_2O_3 + 3O_2.$$

It is soluble in water, with which it combines, furnishing the ions $CrO_4^{--}$, $Cr_2O_7^{--}$, $Cr_3O_{10}^{--}$, $Cr_4O_{13}^{--}$

$$CrO_3 + H_2O \rightleftharpoons 2H^+ + CrO_4^{--}$$
$$2CrO_4^{--} + 2H^+ \rightleftharpoons Cr_2O_7^{--} + H_2O.$$
$$CrO_4^{--} + Cr_2O_7^{--} + 2H^+ \rightleftharpoons Cr_3O_{10}^{--} + H_2O$$
$$CrO_4^{--} + Cr_3O_{10}^{--} + 2H^+ \rightleftharpoons Cr_4O_{13}^{--} + H_2O$$

Thus in presence of acids ($H^+$) solutions of chromic anhydride form the orange dichromate ion together with the dark red trichromate and tetrachromate ion, while alkalis produce the yellow chromate ion. It should be noted that chromic acid $H_2CrO_4$ cannot be isolated, though the name is often given to solutions of chromium trioxide.

The oxide is soluble in acetic acid and in ether. In solution in the former solvent it is a valuable oxidising agent in organic chemical practice.

The oxidising powers of chromium trioxide are considerable.

Alcohol bursts into flame when dropped upon it, and it oxidises all the ordinary oxidisable materials.

These reactions are discussed under potassium dichromate.

**987. Potassium Chromate and Dichromate.**—These salts—the most important compounds of chromium—are manufactured direct from chrome iron ore. The ore, which is very hard, is stamped to fine powder and mixed with anhydrous sodium carbonate and lime. The mixture is heated to *c.* 1,400° C., in presence of a good supply of air, and extracted with water and a little sulphuric acid,

$$4Na_2CO_3 + 2Cr_2O_3 + 3O_2 = 4Na_2CrO_4 + 4CO_2.$$

The iron of the ore is left behind as oxide. The product is extracted with water and concentrated. A slight excess of sulphuric acid is added, giving sodium dichromate,

$$2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O.$$

Potassium dichromate is prepared by adding potassium chloride to the concentrated solution of sodium dichromate, prepared as above. Since potassium dichromate is much less soluble than the other salts present, it crystallises on cooling. It is usually recrystallised.

**988. Potassium Chromate $K_2CrO_4$** may be prepared by adding potassium hydroxide solution to the dichromate

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$$

It forms lemon-yellow crystals, very soluble in water (62 gms. at 15° C., 79 gms. at 100° C. in 100 gms. water). Both the chromates and dichromates are poisonous and may produce intractable sores on those who work with them continually. When heated it does not decompose. Alkaline or neutral reducing agents reduce it to chromic oxide or hydroxide.

Even weak acids convert it to some extent into dichromate. The reaction is reversible.

$$2CrO_4^{--} + 2H^+ \rightleftharpoons Cr_2O_7^{--} + H_2O.$$

Thus the addition of an acid to a chromate changes it from yellow chromate to orange dichromate, while the addition of an alkali, by removing hydrion, changes the orange dichromate to the yellow chromate.

Potassium chromate is not much used in industry or the laboratory, the dichromate being more efficient for most purposes. It is, however, used in testing for lead salts, which give a brilliant yellow precipitate of lead chromate,

$$Pb^{++} + CrO_4^{--} = PbCrO_4\downarrow$$

and as an indicator in the titration of silver nitrate with chlorides, red silver chromate being precipitated as soon as all the chloride present has been converted into white silver chloride (§ 321).

**989. Potassium Dichromate $K_2Cr_2O_7$.**—This salt crystallises in large red tabular crystals. It melts at about 400° C., and on cooling solidifies to a mass which breaks up into small crystals. The best way to powder potassium dichromate is therefore to melt it and let it solidify, when the resulting solid can be ground up with great ease. It is moderately soluble in cold water (10 gms. per 100 c.c. water at 15° C.), and freely soluble in hot water 94 gms. per 100 c.c. water at 100° C.).

Potassium dichromate is an excellent oxidising agent. The general reactions for its oxidising action are :—

(1) When acid is not present,

$$K_2Cr_2O_7 + 4H_2O + 3X = 2KOH + 2Cr(OH)_3 + 3XO$$

(2) In acid solution,

$$K_2Cr_2O_7 + 5H_2SO_4 + 3X = 2KHSO_4 + Cr_2(SO_4)_3 + 4H_2O + 3XO,$$

or $$Cr_2O_7^{--} + 8H^+ + 3X = 2Cr^{+++} + 4H_2O + 3XO.$$

Among its oxidising actions may be mentioned the oxidation of the hydrogen halides to halogen and water, sulphur dioxide to sulphuric acid, hydrogen sulphide to water and sulphur, alcohol to aldehyde and acetic acid, ferrous salts to ferric salts. The equations for these reactions may be deduced by writing the equations for the reaction of the substance oxidised with three atoms of oxygen and adding it to the general reaction as given above. Thus in the last case we may write,

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O$$

$$\therefore \quad 6FeSO_4 + 3H_2SO_4 + 3O = 3Fe_2(SO_4)_3 + 3H_2O$$

General equation,

$$\underline{K_2Cr_2O_7 + 5H_2SO_4 = 2KHSO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O}$$

Adding, and deducting the 3O from each side, we obtain

$$6FeSO_4 + 8H_2SO_4 + K_2Cr_2O_7 = 2KHSO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3.$$

The operation is more simply performed by ionic equations,

$$2Fe^{++} + 2H^+ + O = 2Fe^{+++} + H_2O$$

$$\therefore \quad 6Fe^{++} + 6H^+ + 3O = 6Fe^{+++} + 3H_2O$$

$$\underline{Cr_2O_7^{--} + 8H^+ = 2Cr^{+++} + 4H_2O + 3O}$$

$$Cr_2O_7^{--} + 6Fe^{++} + 14H^+ = 6Fe^{+++} + 2Cr^{+++} + 7H_2O$$

As a second example we may take its reaction with sulphur dioxide

$$3SO_2 + 3H_2O + 3O = 3H_2SO_4.$$

$$\frac{K_2Cr_2O_7 + 5H_2SO_4 = 2KHSO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O}{K_2Cr_2O_7 + 2H_2SO_4 + 3SO_2 = 2KHSO_4 + Cr_2(SO_4)_3 + H_2O.}$$

Potassium dichromate in contact with organic matter is sensitive to light. A mixture of gelatine, potassium dichromate and an insoluble pigment is used in the sensitive tissue employed in the 'Carbon Process' of photography. When exposed under a negative the portions exposed to light—the shadows—become insoluble in water while the protected portions are not affected. Careful treatment of the tissue with warm water washes away these latter, leaving the white foundation paper, but does not affect the parts which light has rendered insoluble.

**989a. Potassium Trichromate $K_2Cr_3O_{10}$** and **Potassium Tetrachromate $K_2Cr_4O_{13}$** can be crystallised from solutions containing suitable proportions of chromium trioxide and potassium dichromate. They are dark red-brown salts.

**990. Sodium Dichromate** is sometimes used in preference to the potassium salt, since it is far more soluble in water, 109 gms. of the salt dissolving in 100 gms. of water at 15°C.

**991. Lead Chromate $PbCrO_4$** is insoluble in water and is made by mixing a solution of a lead salt with that of a chromate,

$$Pb^{++} + CrO_4^{--} \rightleftharpoons PbCrO_4\downarrow$$

Lead chromate is a bright yellow powder much used as a pigment under the name of 'chrome yellow.' Basic lead chromate is red in colour and is also a valuable pigment. It is formed by treating lead chromate with lime.

Barium and zinc chromates have both been used as yellow pigments. They lack the fine covering power of chrome yellow, but are not blackened by hydrogen sulphide.

**992. Ammonium Dichromate $(NH_4)_2Cr_2O_7$** forms orange crystals which, when heated, decompose, forming a very voluminous mass of chromium sesquioxide and evolving nitrogen (§ 679) and steam,

$$(NH_4)_2Cr_2O_7 = N_2 + 4H_2O + Cr_2O_3.$$

The salt only requires to be lighted with a match to bring about its somewhat spectacular decomposition.

**993. Chromyl Chloride $CrO_2Cl_2$.**—This interesting substance is an acid chloride analogous to sulphuryl chloride $SO_2Cl_2$. It is evolved as a red vapour when sulphuric acid acts on a mixture of potassium dichromate and a chloride, such as common salt,

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 = 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O.$$

It is a deep-red liquid evolving a red vapour. It boils at 116° C.

Added to water it decomposes, yielding chromium trioxide and hydrochloric acid.

$$CrO_2Cl_2 + H_2O = CrO_3 + 2HCl.$$

Bromides and iodides when heated with sulphuric acid and a dichromate yield only the free halogen and not a chromyl compound. So to test for chloride in presence of bromide and iodide, the material is heated with a dichromate and sulphuric acid and the vapours led into water. The solution is boiled to remove bromine and iodine and then tested for chromate. If this is found a chloride must have been present.

**994. Potassium Chlorochromate $KCrO_3Cl$** is derived from an acid analogous to chlorsulphonic acid (§ 952). This acid does not exist in the free state. It is made by dissolving 50 gms. of potassium dichromate in a mixture of 65 c.c. concentrated hydrochloric acid and 50 c.c. water without too much heating, and allowing the mixture to cool. It forms fine orange-red crystals. These decompose when gently heated,

$$4KCrO_3Cl = K_2Cr_2O_7 + Cr_2O_3 + 2KCl + Cl_2 + O_2.$$

Heated with sulphuric acid it gives chromyl chloride.

**995. Perchromic Acid.**—Several perchromic acids exist. The blue substance, formed by the action of hydrogen peroxide on an acid solution of a dichromate, was formerly thought to be perchromic acid $H_3CrO_8$, but recent work indicates that it may be a peroxide $CrO_5$,

$$CrO_3 + 2H_2O_2 = CrO_5 + 2H_2O.$$

The deep blue solution decomposes in a few seconds, but if it is shaken with ether the blue compound dissolves in the ethereal layer and is then fairly stable. On standing in acid solution it forms chromic salts and oxygen.

Perchromates are certainly formed by the action of hydrogen peroxide on alkaline solutions of chromates. Their formulæ are not definitely settled.

### Salts of Chromium

**996. Chromous Salts.**—These salts, in which chromium is bivalent have a blue colour, somewhat more violet in tint than that of copper salts. They are all powerful reducing agents, being readily oxidised to chromic salts,

$$2CrCl_2 + 2HCl + O = 2CrCl_3 + H_2O$$
$$2Cr^{++} + 2H^{+} + O = 2Cr^{+++} + H_2O.$$

They are oxidised by atmospheric air and by almost all oxidising agents and, as they are not readily preserved from oxidation they are made when required,

*Anhydrous Chromous chloride* is made by heating chromic chloride in a current of dry hydrogen. It is a white powder.

$$H_2 + 2CrCl_3 = 2HCl + 2CrCl_2.$$

The hydrated salt is made by adding to chromous acetate, prepared as described below, the minimum quantity of concentrated hydrochloric acid needed to dissolve it, cooling to 0° C., and saturating with hydrogen chloride. It forms sky-blue crystals, which dissolve to a blue solution, having the reducing properties of chromous salts.

*Chromous sulphate* $CrSO_4.7H_2O$ is usually prepared by the action of dilute sulphuric acid on chromous acetate (*v. infra*). It forms blue crystals, isomorphous with ferrous sulphate.

*Chromous acetate*, which is sparingly soluble, is readily made by the vigorous reduction of dichromates or chromic salts. A good method consists of reducing a solution of potassium dichromate with pure zinc and hydrochloric acid in a flask with cork and tubes arranged as in Fig. 195. One part of solid powdered potassium dichromate and 6 parts of pure zinc are placed in a flask, the cork is removed, and 5 parts of a mixture of equal proportions of hydrochloric acid and water are added. When the violent reaction has subsided and the liquid is bright blue, the solution is blown by a stream of carbon dioxide through an asbestos or glass-wool filter into a solution of sodium acetate. The zinc chloride is not precipitated, but the sparingly soluble chromous acetate comes down as red crystals, which may be filtered off and dried *in vacuo*, or in a current of an inert gas,

$$CrCl_3 + H = CrCl_2 + HCl$$

$$CrCl_2 + 2Na\bar{A} + H_2O = Cr\bar{A}_2.H_2O + 2NaCl.$$

Chromous acetate is the starting point for the preparation of the other chromous salts.

**997. Chromic Salts.**—These, though at first sight resembling those of the other metals, are actually peculiar in their composition and behaviour.

It has been found that some chromic salts are only partly ionised. They exist, too, in two modifications, green and violet, which behave differently towards various reagents.

Thus, when green chromic chloride solution is mixed with silver nitrate solution only *one-third* of the chlorine is precipitated as silver chloride, the reaction *apparently* being

$$CrCl_3 + AgNO_3 = CrCl_2NO_3 + AgCl,$$

not as would be expected,

$$CrCl_3 + 3AgNO_3 = Cr(NO_3)_3 + 3AgCl.$$

Again, chromic sulphate as obtained by the reaction of sulphur dioxide with chromic acid (cf. § 989) at — 4° C., gives no precipitate with barium chloride and therefore yields no sulphate ion. Other sulphates, all having the apparent formula $Cr_2(SO_4)_3$, precipitate one-third or two-thirds of their sulphate.

These salts obviously differ from the ordinary metallic salts in some way and the solution of the problem has been found by the study of the remarkable complex chromium compounds which are formed with ammonia, cyanides, etc.

In brief, chromium forms a series of compounds, usually complex ions, by combination with *six* other groupings of atoms. These latter may be whole molecules, monovalent atoms, etc.

The character of the grouping is determined by the number of electronegative or electropositive groupings it contains. The charge on the whole group is the sum of its constituent charges. Thus the grouping

$$[Cr^{+++}(Cl^-)_2(H_2O)_4]$$

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has a single positive charge and the grouping

$$[Cr(Cl_3)(H_2O)_3]$$

has no charge and does not behave like an ion at all. The matter is further explained in §§ 999, 1235–1238.

**998. Chromic Chloride $CrCl_3$.**—This salt exists :—

(1) as the pinkish-violet anhydrous salt, $CrCl_3$.

(2) as the green hydrated salt $CrCl_3 . 6H_2O$.

(3) as the violet hydrated salt, also $CrCl_3 . 6H_2O$.

The anhydrous salt is made in various ways, as, for example, by the action of chlorine on the metal, but most easily by the action of sulphur chloride vapour on chromium sesquioxide,

$$6S_2Cl_2 + 2Cr_2O_3 = 4CrCl_3 + 3SO_2 + 9S.$$

The anhydrous chloride so obtained is hardly soluble in water unless a trace of the green chromic salt is present.

A green hydrated salt is obtained by the action of hydrochloric acid on chromic hydroxide. It forms a very deliquescent green mass. The pure green form is, however, best made by reducing chromates with hydrochloric acid and precipitating the salt by saturation with hydrogen chloride. The pure violet form can be made by heating a 50 per cent. solution of the green form to 80° C., cooling to 0° C. and saturating with hydrogen chloride.

In solution both forms coexist in equilibrium. In dilute solution the violet form predominates and in strong solution the green.

A solution of the violet compound when treated with silver nitrate solution precipitates all its chlorine as silver chloride ; a solution of the green compound only precipitates one-third of its chlorine in this way. It is presumed then that only one-third of the chlorine in the latter is combined as in a true salt by an electro-valent linkage, and the two compounds, both of which have the empirical formula $CrCl_3 . 6H_2O$, are believed to have the structure

| Violet | Green |
|---|---|
| $[Cr(H_2O)_6]Cl_3$ | $[Cr(H_2O)_4Cl_2]Cl . 2H_2O$. |

The portions enclosed in the square brackets function as single groups, and, just as the cyanide groups in potassium ferrocyanide $K_4[Fe(CN)_6]$ do not give the reactions of a cyanide, so the chlorine atoms enclosed in the bracket in the formula $[Cr(H_2O)_4Cl_2]Cl$ do not display the usual properties of chlorides. This view is confirmed by the fact that the conductivity of the green form is less, indicating that it forms fewer ions. The lowering of the freezing point of water by the violet form is about twice that caused by the same proportion of the green form, also indicating that twice as many ions are given by the former. Finally the green form readily loses two

molecules of water in the desiccator while the violet form loses none

A third light-green hydrated form has been prepared and seems to be $[Cr(H_2O)_5Cl]Cl_2.H_2O$.

**999. Chromic Sulphate $Cr_2(SO_4)_3$.**—The anhydrous salt forms bluish-red crystals. As in the case of chromic chloride (§ 998) there are violet and green hydrates. The latter are abnormal in behaviour, one hydrate, formed by saturating chromic acid with sulphur dioxide at — 4° C., not giving, when freshly prepared, any precipitate with barium chloride.

A second green hydrate precipitates two-thirds of its sulphate, and another one-third under these circumstances. The violet hydrate behaves normally.

The compositions of these hydrates are probably,

$$\left[Cr_2{}^{(SO_4)_3}_{(H_2O)_6}\right]$$

Not precipitated by $BaCl_2$.

$$\left[Cr_2{}^{(SO_4)}_{(H_2O)_{10}}\right][SO_4]_2.$$

Two-thirds of the 'sulphate' precipitated by barium chloride.

$$\left[Cr_2{}^{(SO_4)_2}_{(H_2O)_8}\right]SO_4.$$

One-third of the 'sulphate' precipitated by barium chloride.

Solutions of chromium sulphate probably contain all of these isomeric forms.

A simple experiment will illustrate the peculiar character of these salts. If equal quantities of cold sulphur dioxide solution be oxidised (*a*) by chromic acid, (*b*) by potassium permanganate, the solution of chromium sulphate gives only a slight precipitate with barium chloride, while the solution of potassium and manganese sulphate gives a dense white precipitate.

**1000. Chrome Alum, Potassium Chromium Alum, $K_2SO_4.Cr_2(SO_4)_3 24H_2O$ or $KCr(SO_4)_2 . 12H_2O$.**—This, the commonest of the chromic salts, is readily obtained by reducing a solution of potassium dichromate and sulphuric acid with sulphur dioxide, oxalic acid, etc.

It may be prepared in fine octahedra by dissolving 40 gms. of potassium dichromate in 120 c.c. of water and adding 10 gms. of concentrated sulphuric acid. The solution is cooled and saturated with sulphur dioxide until a test portion smells of the gas after standing. The alum crystallises on cooling.

Chrome alum forms fine octahedra of a deep violet colour and isomorphous with the other alums (§ 938). The salt is soluble in water, 100 gms. of which dissolve 24·4 gms. of chrome alum at 25° C. The solution is violet, but when heated to about 60° C. becomes green. The green solutions crystallise only with difficulty.

Chrome alum behaves in general like a mixture of chromium and potassium sulphates.

It finds a use in industry as a mordant in dyeing and also for tanning leather.

*Sodium chrome alum* $NaCr(SO_4)_2 12H_2O$ and *ammonium chrome alum* $NH_4Cr(SO_4)_2 12H_2O$ are also known.

**1001. Chromic Sulphide $Cr_2S_3$** is not formed by the action of hydrogen sulphide on chromic salts. It may be made by the action of hydrogen sulphide on red-hot chromic oxide,

$$Cr_2O_3 + 3H_2S = Cr_2S_3 + 3H_2O.$$

**1002. Chromic Cyanide $Cr(CN)_3$** is a greenish-blue powder. Derived from it are a series of chromicyanides, such as $K_3[Cr(CN)_6]$, analogous to the ferricyanides, which they resemble.

**1003. Detection and Estimation of Chromium.**—The simplest test for a chromium compound is to mix it on broken porcelain with excess of sodium carbonate and a crystal of potassium nitrate and heat strongly. Chromium compounds form a yellow mass of chromate which dissolves to a yellow solution which, when acidified with acetic acid and mixed with barium chloride, gives a light yellow precipitate of barium chromate.

In solution chromium compounds may be added to a gently warmed mixture of caustic soda and hydrogen peroxide. This converts them to chromates,

$$Cr_2(SO_4)_3 + 6NaOH = 2Cr(OH)_3 + 3Na_2SO_4$$
$$2Cr(OH)_3 + 3H_2O + 4NaOH = 2Na_2CrO_4 + 8H_2O,$$

which are detected by their yellow colour and also as below.

Chromates are readily detected by their formation of the deep blue perchromic acid or chromium peroxide (§ 995). The cold solution containing the chromate acidified with sulphuric acid is covered with about 1 cm. depth of ether and an excess of hydrogen peroxide is added and the mixture is shaken. The deep blue peroxide dissolves in the ethereal layer. The test is a very sensitive one.

**1004. Estimation.**—Chromium, in the form of dichromate or chromate, may be estimated by titration with ferrous sulphate solution or, better, by adding a measured portion of an acidified solution containing the chromate to an excess of potassium iodide. The solution is then nearly neutralised and the liberated iodine is titrated with sodium thiosulphate,

$$CrO_4^{--} + 3I^- + 8H^+ = Cr^{+++} + 3I + 4H_2O$$
$$Cr_2O_7^{--} + 6I^- + 14H^+ = 2Cr^{+++} + 6I + 7H_2O$$

In each case one chromium atom corresponds to three iodine atoms.

If the chromium is present as chromic salt it may be oxidised with sodium hydroxide and hydrogen peroxide, any excess of the latter

being removed by boiling. This solution can be acidified and treated as above.

Alternatively, chromium may be determined gravimetrically by precipitating it with ammonia as chromic hydroxide, igniting this and weighing as oxide.

The precipitate of chromium hydroxide so obtained is very slow to filter, and a more granular precipitate is obtained by boiling the chromium salt with, say, a nitrite,

$$3KNO_2 + CrCl_3 \rightleftharpoons Cr(NO_2)_3 + 3KCl$$
$$Cr(NO_2)_3 + 3H_2O = Cr(OH)_3 \downarrow + 3HNO_2.$$

## MOLYBDENUM Mo, 95·95

The element molybdenum, in its general behaviour, resembles chromium. Its compounds are, however, less acidic in character and have, perhaps, an even greater tendency to form complex compounds.

**1005. Occurrence.**—The commonest ore of molybdenum is molybdenite $MoS_2$. This was confused with graphite and galena, and the name molybdenite (derived from the Greek *μόλυβδος*, molybdos, lead) arises from this error.

**1006. Extraction.**—Molybdenite may be roasted, forming the crude trioxide which is converted by ammonia into ammonium molybdate. This, on heating, yields pure molybdenum trioxide, which may be reduced with aluminium powder as described under chromium (§ 978).

**1007. Properties.**—Molybdenum is a moderately hard white metal. It melts at the very high temperature of 2,450° C. Its density is 10·28.

Molybdenum is oxidised slowly by air at a red heat to the trioxide

$$2Mo + 3O_2 = 2MoO_3.$$

Chlorine attacks it at a red heat.

The action of acids upon it is slow, but it is attacked by hydrochloric acid, by nitric acid and by hot concentrated sulphuric acid.

Molybdenum is now a metal of industrial importance, some 250,000 tons of molybdenum steel being produced yearly. Metallic molybdenum is strong and has a very high fusing point. It is used for the supporting wires for the filaments in glow lamps; also as windings for resistance furnaces. Steel containing some 0·15 per cent. of molybdenum, together with a somewhat larger proportion of chromium and manganese, is valuable as being of great strength and not being weakened by moderate degrees of heat. It is useful as a tool steel (cf. p. 679) and also for parts of structures built up by

welding. An alloy known as stellite is used for high-speed lathe tools, which are required to retain their cutting powers up to a red heat. A typical specimen might contain 20 per cent. of molybdenum, 60 per cent. of cobalt, 10 per cent. of chromium, and 10 per cent. of other metals, iron, manganese, etc.

**1008. Molybdenum Oxides.**—Five oxides, $Mo_2O_3$, $MoO_2$, $Mo_3O_8$, $Mo_2O_5$ and $MoO_3$ exist.

*Molybdenum sesquioxide* $Mo_2O_3$ is basic in character.

*Molybdenum dioxide* $MoO_2$ is probably complex in character, not being attacked by solutions of acids or of alkalies.

*Blue molybdenum oxide* $Mo_3O_8$ is interesting as being colloidal. It is obtained by the action of powdered molybdenum on a solution of molybdenum trioxide. It is a dark blue substance, dissolving to a blue colloidal solution. It has been used as a dye for silk and as a pigment for colouring india-rubber.

**1009. Molybdenum Trioxide $MoO_3$** is prepared by roasting molybdenite $MoS_2$,

$$2MoS_2 + 7O_2 = 2MoO_3 + 4SO_2.$$

The oxide is purified by dissolving it in ammonia, forming ammonium molybdate, removing copper, which also dissolves, with ammonium sulphide and igniting the ammonium molybdate.

Molybdenum trioxide is a white powder, which becomes yellow when heated. It is soluble in water to a slight extent, forming an acid solution. It is much less strongly acidic than chromium trioxide. With alkalis it forms the *molybdates*.

*Molybdic acid* $H_2MoO_4$ can be prepared by the action of nitric acid on ammonium molybdate under certain conditions.

*The Molybdates.*—Few of these have the simple formula $X_2MoO_4$, where X is a univalent metal. These normal molybdates readily form complex polymolybdates. Thus the only common molybdate, ammonium molybdate, has the formula $(NH_4)_6Mo_7O_{24}.4H_2O$. At least four other ammonium molybdates exist but are not commonly met with. In all groups of the Periodic table the oxyacids become more complex as the atomic weight increases.

The chief interest of ammonium molybdate is its use in detecting and estimating phosphorus. With solutions of phosphates it forms the yellow insoluble ammonium phospho-molybdate. The method is described under phosphorus (§ 785).

**1010. Salts of Molybdenum.**—No true salts of molybdenum are known. Chlorides of formula $MoCl_2$, $MoCl_3$, $MoCl_4$, $MoCl_5$, are known. They either form complex ions, as $MoCl_2$ and $MoCl_3$, or are volatile covalent compounds.

Molybdenum sulphate is of doubtful existence, but an oxysulphate, $Mo_2O(SO_4)_2.xH_2O$, is known. No other salts of molybdenum exist.

## TUNGSTEN W, 183·92

**1011. Tungsten, extraction and properties.**—The most important mineral of tungsten is *Wolframite*, a mixture of iron and manganese tungstates (Fe, Mn)$WO_4$ and *Scheelite*, calcium tungstate $CaWO_4$.

Wolframite is decidedly magnetic and is separated by an electromagnetic separator from the tin ores with which it is usually

associated. In a simple type of magnetic separator the pulverised ore falls off a belt under the influence of a strong magnetic field, and is separated into two streams of particles, which collect into separate heaps, that containing the tungsten being the nearest to the magnet.

*Scheelite*, calcium tungstate $CaWO_4$, is also a widely distributed ore.

*Extraction.*—Wolframite may be roasted with alkali, when the reaction

$$12FeWO_4 + 5Na_2CO_3 = 12FeO + 5CO_2 + Na_{10}W_{12}O_{41},$$

occurs. The soluble tungstate is dissolved out and treated with acid, when tungstic anhydride $WO_3$ is obtained.

This is reduced in various ways, with carbon, zinc, aluminium, or calcium.

The metal is obtained in the state of powder and, being required as fine wire for the purpose of glow-lamp filaments, has to be got into a compact condition. As its melting point is about 3,300° C. it is impossible to make it compact by fusion.

The powder is subjected to great pressure in a hydraulic press and is thus converted into bars which are compact enough to handle. These are heated to a high temperature in an atmosphere of hydrogen ; the effect of this process is to make them strong but brittle. The metal is then mechanically hammered *in vacuo* at a temperature of about 1,500° C. It is then sufficiently tough to be drawn into fine wire.

Very fine tungsten wire is used in the manufacture of electric lamps. The value of tungsten for glow-lamp filaments is due to its very high melting point, and its very slight volatility at high temperatures. The filament may be heated to about 2,100° C., but at higher temperatures it volatilises and blackens the glass of the lamp. If the lamps are filled with nitrogen or argon the increased pressure diminishes the volatilisation and the filaments may be made hotter, thus giving out a greater proportion of their radiant energy as light and less as radiant heat.

Tungsten is a hard silver-white metal. It has the very high density of 19·3, and the remarkable melting point of 3,267 $\pm$ 30°C.,[1] higher than that of any other element except carbon.

Tungsten is not oxidised below a bright red heat. It is attacked by chlorine at a red heat. Acids hardly attack the metal, even aqua regia having little or no effect. The resistance is due to the formation of a coating of oxide.

[1] As might be expected, the figures given for so high a melting point are not altogether consistent.

Oxidising agents, such as fused potassium chlorate, oxidise it vigorously.

Tungsten finds uses for electric lamp filaments, and as a substitute for platinum in electrical work where sparking is to be expected (switches, make-and-break contacts, etc.). Steel containing some 16–20 per cent. of tungsten together with 3–5 per cent. of chromium is very hard and strong, and retains its temper at very high temperatures. It is therefore valuable for the cutting edges of high-speed lathe-tools.

**1012. Oxides of Tungsten.**—Tungsten forms three oxides, $WO_2$, $W_2O_5$, $WO_3$.

*Tungsten dioxide* $WO_2$ is obtained by reducing the trioxide with hydrogen. It is a powerful reducing agent. It appears to be basic but forms no well-defined salts.

Blue tungsten oxide $W_2O_5$ resembles the blue oxide of molybdenum in forming colloidal solutions.

*Tungsten trioxide, tungstic anhydride* $WO_3$, is best made by treating native calcium tungstate with concentrated hydrochloric acid, filtering off, re-dissolving the oxide in ammonia and evaporating to dryness,

$$CaWO_4 + 2HCl = CaCl_2 + H_2WO_4.$$
$$(NH_4)_{10}W_{12}O_{41} = 12WO_3 + 10NH_3 + 5H_2O.$$

It is a yellow powder insoluble in water and acids, but soluble in alkalis, forming tungstates.

**1013. Tungstic Acid $H_2WO_4$** is made by the action of hydrochloric acid on a tungstate. It is insoluble in water but forms colloidal sols. The tungstates resemble the molybdates.

*Sodium para-tungstate* is an article of commerce, and has the formula $Na_{10}W_{12}O_{41}$ or $5Na_2O.12WO_3$. It has been used for rendering cotton, etc., non-inflammable.

**1014. Tungsten Compounds.**—Like molybdenum, tungsten forms no true salts. The dichloride $WCl_2$ is polymerised in solution. The higher chlorides, $WCl_4$, $WCl_5$, $WCl_6$, are all decomposed by water. The sulphide, $WS_2$, is found as a soft black mineral. Various phosphides, borides and carbides exist.

*Tungsten Carbide WC* is used industrially for making the tips of lathe-tools. It is intensely hard and retains its hardness at a high temperature, so permitting a high cutting speed.

## URANIUM U, 238·07

The element uranium is interesting as being the element of the highest known atomic weight, and being the parent substance of a large number of radio-elements (*v.* § 1259).

**1015. Occurrence.**—Uranium occurs as uranium oxide $U_3O_8$ in *pitchblende*, as potassium uranyl orthovanadate $K.UO_2(VO_4).3H_2O$, *carnotite*, and as calcium uranyl phosphate in *autunite* $Ca(UO_2)_2(PO_4)_2.8H_2O$, and in several other minerals. These ores are now of

great value, since they are the source of radium, for which a great demand exists.

**1016. Preparation.**—Uranium is best made by heating a mixture of the oxide $U_3O_8$ with aluminium. It may be prepared in a purer condition by the action of sodium on uranous chloride in a steel bomb.

**1017. Properties.**—When compact it forms a white lustrous metal, but as obtained by reduction forms a black powder. Its melting point is about 1,800° C. Its density is 18·5.

The element is fairly reactive, particularly when finely-divided. The powder burns in air, reacts with the halogens and sulphur and is attacked by acids. It appears to be rather less electropositive than copper.

**1018. Atomic Weight of Uranium.**—Until Mendeléeff formulated his Periodic table uranium was thought to have the atomic weight of 120 (O = 16). There was no place for such an element, and Mendeléeff suggested the value 240 and the placing of the element with chromium, molybdenum and tungsten, to which elements it was chemically similar. The correctness of this value was confirmed by the Dulong and Petit's law, and by the determination of the vapour densities of some of its halides. The most accurate determinations carried out by converting uranous bromide $UBr_4$ into silver bromide 4AgBr, gave the ratio $UBr_4 : 4AgBr$, from which U = 238·19. The value 238·07 is accepted. The value is interesting as being the highest atomic weight and also as being the atomic weight of a parent radio-element.

**1019. Uranium Oxides.**—There appear to be four oxides of uranium, $UO_2$, $U_2O_5$, $U_3O_8$, $UO_3$.

*Uranous oxide* $UO_2$ is made by heating sodium uranate with common salt and charcoal, or by reducing the green oxide, $U_3O_8$, in a current of hydrogen. It is soluble in acids only with difficulty, and acts as a strong reducing agent. It was for long, like the oxide of vanadium VO, thought to be the metal itself.

*Urano-uranic oxide, green oxide of uranium,* $U_3O_8$, is found in Nature as pitchblende. It is made by heating any of the other oxides to a strong red heat in oxygen, or by heating uranyl acetate.

It is attacked by acids only with difficulty.

*Uranium trioxide* $UO_3$ is yellow or reddish in colour. It may be prepared by heating uranyl nitrate in a current of oxygen at 500° C.,

$$2UO_2(NO_3)_2 = 2UO_3 + 4NO_2 + O_2.$$

It is amphoteric in character, forming uranates with alkalis and uranyl salts (*q.v.*) with acids.

*The uranates* are well-defined salts of greenish yellow to reddish yellow colour.

*Sodium di-uranate* $Na_2U_2O_7.6H_2O$ is prepared by adding caustic soda to a uranyl salt ; it is almost insoluble in water,

$$2UO_2(NO_3)_2 + 6NaOH = Na_2U_2O_7 + 3H_2O + 4NaNO_3.$$

The hexahydrated salt is known as *uranium yellow* and is used in colouring glass and porcelain.

**1020. Salts of Uranium.**—There are two series of uranium salts, the *uranous* salts in which uranium is tetravalent, as in uranous

chloride $UCl_4$; and the *uranyl* salts, in which the basic radical is the divalent grouping $UO_2$,$^{++}$ as in uranyl nitrate $UO_2(NO_3)_2$.

The salts commonly met with are those of the latter series.

**1021. Uranous Salts** are unstable and readily oxidised to uranyl salts They are therefore reducing agents.

*Uranous chloride* $UCl_4$ is a dark green solid obtained by heating uranium in a stream of chlorine. It is a powerful reducing agent, forming uranyl chloride.

*Uranous sulphate* $U(SO_4)_2 4H_2O$ is prepared by the reducing action of alcohol on uranyl sulphate solution containing sulphuric acid,

$$UO_2(SO_4) + H_2SO_4 = U(SO_4)_2 + H_2O + O.$$

*Uranous nitrate* does not appear to exist.

**1022. Uranyl Salts**—These salts are obtained by the action of the appropriate acid on uranium trioxide,

$$UO_3 + 2HX = UO_2X_2 + H_2O.$$

The basic radical $(UO_2)^{++}$ reacts as a whole in the same way as does $(NH_4)^{+}$ or other compound basic radical.

The uranyl salts are remarkable for their *fluorescence*. Viewed by transmitted light their solutions appear pale yellow, but seen against a dark background they have a fine luminous greenish colour. The term *fluorescent* is used to describe a substance which emits light of a colour not present in the illuminating radiation. Thus uranium salts in solution emit a green light although they may be illuminated, e.g. by a pure blue light containing no waves of the length corresponding to 'green.' The light is emitted usually, but not invariably, of longer wavelength than the light incident on the fluorescent substance.

They are also affected chemically by light, for mixtures of uranyl salts and oxidisable organic substances react in the light.

Thus uranyl chloride and alcohol, when illuminated, give uranous chloride and aldehyde,

$$UO_2Cl_2 + 2HCl + C_2H_5OH = UCl_4 + CH_3.CHO + 2H_2O.$$

Uranyl salts are strongly poisonous.

**1023. Uranyl Chloride $UO_2Cl_2$** may be made by the action of hydrochloric acid on uranium trioxide $UO_3$,

$$UO_3 + 2HCl = UO_2Cl_2 + H_2O,$$

or by the action of chlorine on uranium dioxide. This latter reaction again shows the resemblance of the dioxide to a metal. It is a yellowish green crystalline substance very soluble in water. The solution is slowly hydrolysed, depositing uranic hydroxide. It forms well-marked double salts, such as potassium uranyl chloride $K_2(UO_2)Cl_4$.

**1024. Uranyl Sulphate $UO_2SO_4$** is obtained by the action of sulphuric acid on urano-uranic oxide, the uranous sulphate also formed being oxidised by nitric acid,

$$U_3O_8 + 4H_2SO_4 = U(SO_4)_2 + 2UO_2SO_4 + 4H_2O$$
$$U(SO_4)_2 + 2HNO_3 = UO_2SO_4 + H_2SO_4 + 2NO_2.$$

It forms yellowish-green fluorescent crystals, which are moderately soluble in water.

**1025. Uranyl Nitrate $UO_2(NO_3)_2 6H_2O$** is the most important uranium compound. It is prepared by the action of nitric acid on any oxide of uranium.

It forms greenish-yellow fluorescent prisms. These have remarkable properties. They are *triboluminescent, i.e.*, they give out flashes of light when crushed, rubbed or shaken. This phenomenon is given to a much smaller degree by sugar, two lumps of which, when rubbed together in the dark, give out a faint light. Uranyl nitrate crystals occasionally explode violently, but this property is due to organic impurity.

Uranyl nitrate is readily soluble in water, which dissolves about twice its weight of the nitrate. When heated, uranyl nitrate gives off water and oxides of nitrogen, leaving uranic acid and uranic anhydride.

**1026. Uranyl Acetate $UO_2(C_2H_3O_2)_2$** has been used as a reagent for the precipitation of sodium. The salt sodium uranyl magnesium acetate is sparingly soluble in water, and on adding a saturated solution of uranyl acetate, mixed with an equivalent proportion of magnesium acetate to a solution of a sodium salt which is not too dilute, a yellowish crystalline precipitate, of composition.

$$NaC_2H_3O_2 \cdot UO_2(C_2H_3O_2)_2 \cdot Mg(C_2H_3O_2)_2 \cdot 9H_2O,$$

gradually separates. Since its crystalline form is easily recognisable under the microscope it affords a means of detecting sodium in small quantities of liquid. The salt sodium uranyl acetate,

$$NaC_2H_3O_2 \cdot UO_2(C_2H_3O_2)_2,$$

is also sparingly soluble and used for the same purpose.

**1027. Radioactive Properties of Uranium.**—The radioactive properties of uranium and the transuranic elements are discussed in Chapter XXVI.

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# CHAPTER XXII

# THE HALOGENS

**1028. The Halogen Group of Elements.**—The elements, fluorine, chlorine, bromine, iodine, and the unstable radioactive astatine, forming the group VII. B in the Periodic table, are known as the *halogens* or " salt-forming " elements, the name arising from the fact that some of them are contained in sea water, which was at one time the chief ultimate source of chlorine, bromine and iodine.

These elements form a very well-marked group, with clearly graded physical and chemical properties, which are further reviewed on p. 735.

Their atomic structure is shown in the accompanying table :—

| Element. | Electrons in Groups possessing | | | | | |
|---|---|---|---|---|---|---|
| | 1 quantum. | 2 quanta. | 3 quanta. | 4 quanta. | 5 quanta. | 6 quanta. |
| Fluorine . | 2 | 7 | | | | |
| Chlorine . | 2 | 8 | 7 | | | |
| Bromine . | 2 | 8 | 18 | 7 | | |
| Iodine . | 2 | 8 | 18 | 18 | 7 | |
| Astatine . | 2 | 8 | 18 | 32 | 18 | 7 |

It will be seen that their atoms are characterised by an outer group of seven valency electrons, which, by receiving a single electron, reach the stable ' inert-gas ' type. Thus they readily form

| Chlorine atom. | Chlorine ion. |
|---|---|
| [2 . 8 . 7] | $[2 . 8 . 8]^-$ |

ions with a single negative charge, $F^-$, $Cl^-$, $Br^-$, $I^-$, and are therefore monovalent in their ionisable compounds, the metallic halides.

They have seven outer electrons, which can be shared with other atoms in their covalent compounds, and accordingly they can show valencies of three, five and seven in these compounds (*e.g.*, $ICl_3$, $I_2O_5$, $Cl_2O_7$).

As the atomic weight becomes greater, the atomic radius becomes larger and the attraction of the positive nucleus exerted upon the outer negative electrons becomes less. Accordingly, fluorine ion $F^-$ is very stable, while iodine ion $I^-$ is very easily oxidised to free iodine

## FLUORINE F, 19·00

**1029. Occurrence.**—The element fluorine is probably found free in minute quantities in a variety of fluorspar found in Bavaria and known as 'Stinkfluss.' Its compounds are not uncommon. These include *fluorspar*, calcium fluoride $CaF_2$, and *cryolite*, sodium aluminium fluoride $3NaF.AlF_3$. Fluorides are found in small quantities in native calcium phosphate (*v.* p. 344). Fluorides are present in the teeth and the element appears to be necessary for animal life.

**1030. Preparation.**—Fluorine has proved itself one of the most difficult elements to isolate. The usual method for preparing chlorine, the oxidation of hydrogen chloride, will not work with hydrogen fluoride. The electrolysis of diluted hydrogen fluoride is useless, for the liberated fluorine attacks the water,

$$2H_2O + 4F = 2H_2F_2 + O_2,$$

and the anhydrous acid is almost a non-conductor of electricity. It is, however, an ionising solvent, like water, and a solution of acid potassium fluoride $KHF_2$ in hydrofluoric acid is a good conductor. Fused potassium hydrogen fluoride also conducts freely. On electrolysis we have fluorine liberated at the anode and potassium and hydrogen at the cathode. The potassium immediately reacts with the hydrogen fluoride and re-forms potassium hydrogen fluoride, which again undergoes electrolysis.

The material for the apparatus presents difficulties, for the fluorine attacks every known substance. Platinum-iridium alloy was at first used, but copper or Monel metal is now employed. This metal becomes coated with an insoluble protective film of copper fluoride $CuF_2$, and then resists further attack. The most reliable method is probably that of Dennis, Veeder and Rochow.

They electrolyse perfectly dry fused potassium hydrogen fluoride $KHF_2$ between graphite electrodes. The reactions are :—

$$KF \rightleftharpoons K^+ + F^-$$

Cathode $\left\{ \begin{array}{r} K + HF = KF + H \\ H + H = H_2 \end{array} \right.$

Anode $F + F = F_2$

It is essential that silicon should be absent from the electrodes and the fluoride, in both of which it is commonly found, since it forms a peculiar poorly-conducting glaze on the former and so slows down the electrolysis. The fluoride must be wholly dry, as even traces of water greatly retard the evolution of fluorine.

The cell is a heavy V-shaped copper tube of 2 inches diameter fitted with copper caps into which the graphite electrodes (300

× 5 mm.) are cemented by Bakelite cement baked at 300° C., which is resistant to fluorine. The cell is heated electrically and lagged with asbestos cement. A current of 5–10 amps. at 12–18 volts

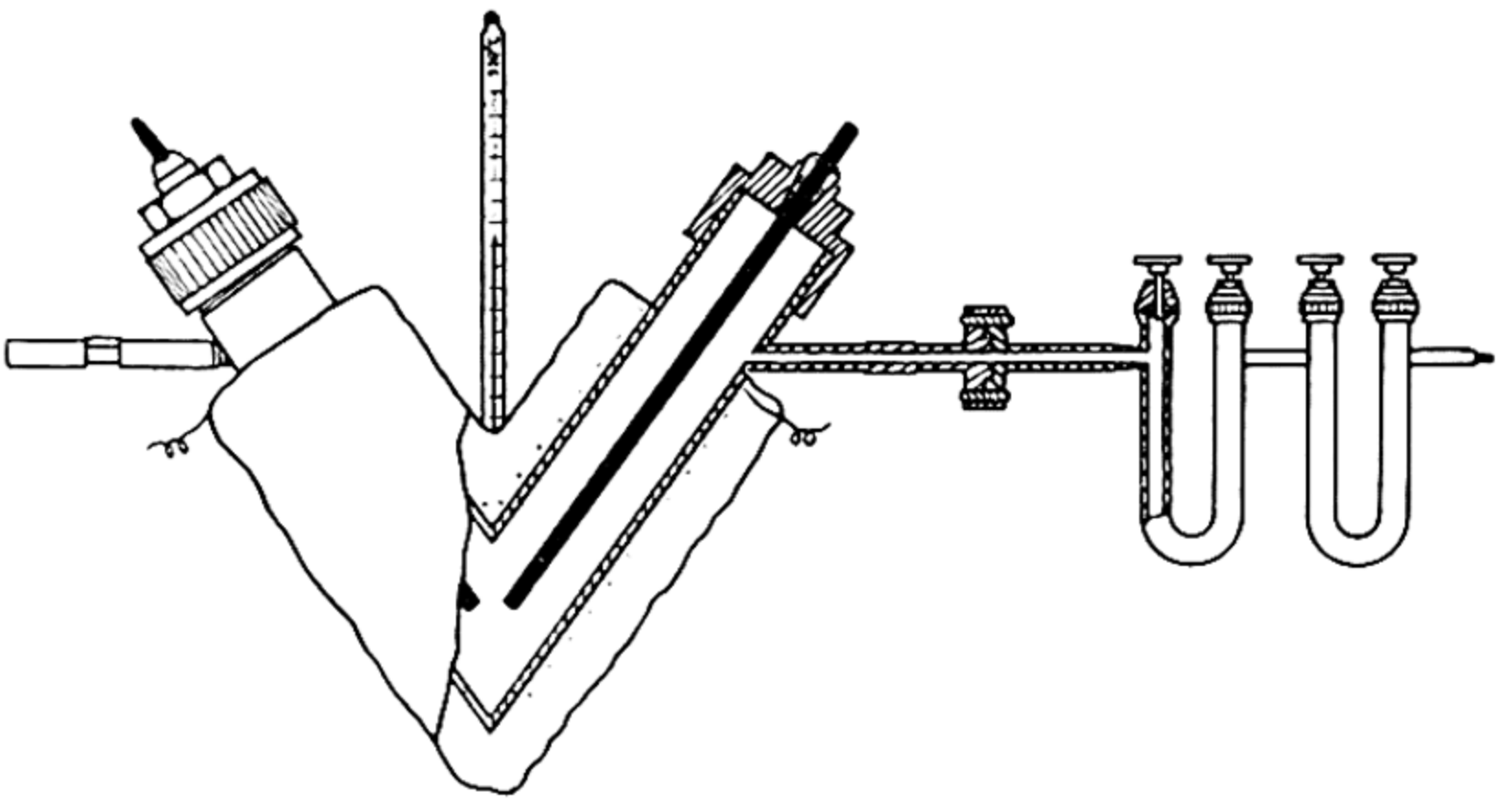


FIG. 172.—Preparation of fluorine.

*(From The Journal of American Chemical Society.)*

gives a free supply of fluorine which is purified from hydrogen fluoride vapour by absorbing the latter in U-tubes filled with sodium fluoride, $NaF + HF = NaHF_2$.

**1031. Properties.**—Fluorine is a pale greenish-yellow gas of penetrating smell not unlike that of chlorine. It has been liquefied and boils at — 184° C. Its density indicates the formula $F_2$.

Fluorine gas is intensely reactive and combines directly with almost all substances except oxygen and nitrogen. It combines with hydrogen with explosion even in the dark, forming hydrofluoric acid. Charcoal takes fire and burns in the gas. Bromine and iodine burn in the gas, as do sulphur, selenium, tellurium, phosphorus, arsenic, silicon and boron. The fluoride formed corresponds as a rule to the highest valency of the element, $SF_6$, $PF_5$, $SiF_4$, etc. Metals are attacked with vigour in most cases in the cold; all metals react if gently heated. The highest fluoride is formed ($CuF_2$, $FeF_3$, $PtF_4$, etc.).

Fluorine also attacks most compounds. Water is decomposed, hydrogen fluoride being formed together with oxygen containing ozone,

$$2F_2 + 2H_2O = 4HF + O_2.$$

All organic compounds are attacked, usually bursting into flame and forming carbon tetrafluoride, hydrogen fluoride, and oxygen. Glass is not attacked if the fluorine is scrupulously freed from hydrogen

fluoride by freezing out all traces with liquid air. Fluorine displaces chlorine from its compounds, forming the fluorides,

$$2KCl + F_2 = 2KF + Cl_2$$
$$CCl_4 + 2F_2 = CF_4 + 2Cl_2.$$

Fluorine acts as an intense oxidising agent. When it is led into an aqueous solution the oxygen produced possesses a degree of chemical energy, which is only paralleled by the oxygen evolved at the anode in a vigorous electrolytic oxidation. Thus it oxidises potassium chlorate $KClO_3$ to the perchlorate $KClO_4$. The gas is accordingly finding some use as an intense oxidising agent.

**1032. Atomic Weight.**—The atomic weight of fluorine has been found by various methods, including among the most accurate the determination of the weight of calcium fluoride to be made from a given weight of calcium oxide. This determination rests on the value given to calcium. The weight of sodium chloride obtained from a given weight of sodium fluoride has also been determined. The value of 19·00 has been adopted.

**1033. Hydrogen Fluoride** $(HF)_x$ is prepared by the action of sulphuric acid on calcium fluoride,

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

On the commercial scale a leaden retort heated on a sand-bath is used and the vapours are conducted into water, so forming a solution of the acid.

To prepare the pure acid in the laboratory, a specimen of potassium hydrogen fluoride $KHF_2$ is dried with scrupulous precautions in a stream of hot well-dried air. It is then distilled in a copper (or platinum) distillation apparatus. The distillate is pure anhydrous hydrogen fluoride and may be collected in a copper bottle cooled in a freezing mixture,

$$2KHF_2 = 2KF + 2HF$$

The pure anhydrous acid does not attack copper, but the solution (commercial hydrofluoric acid) does so and is therefore kept in bottles of gutta-percha or hard paraffin wax (ceresin).

**1034. Properties.**—Hydrofluoric acid is a colourless, very volatile, fuming liquid boiling at 19·5° C. The strong solution (50 per cent.), which is sold commercially, also fumes. The acid is poisonous, its vapour being very injurious to health. The density of its vapour indicates the presence of a certain proportion of polymerised molecules and electron-diffraction studies of the vapour show that numerous polymers $H_3F_3$, $H_4F_4$, $H_5F_5$, etc., are present. Its chemical reactions are most conveniently represented by the formula HF.

The solution of the acid when distilled, if stronger than 37 per cent., loses hydrogen fluoride, but loses water if weaker than 37 per cent. Acid of 37 per cent. strength distils unchanged at 120° C. and

is a constant boiling mixture. Further details are given under hydrochloric acid (§ 1055).

The anhydrous acid shows several points of resemblance to water in its chemical and physical behaviour. Its formula may be taken as intermediate between H – F and $H^+F^-$ (§ 155a) : it is associated and its structure in the liquid state has been written as

$$H^+\left[ :\ddot{F}:H:\ddot{F}: \right]^-.$$

Its boiling point is much higher than that of hydrogen chloride, just as that of water is higher than that of hydrogen sulphide. Both water and hydrogen fluoride are ionising solvents. From the chemical point of view anhydrous hydrofluoric acid combines in a remarkable way with sulphur trioxide and phosphorus pentoxide. It also combines with great vigour with sodium fluoride and potassium fluoride. Compare the reactions,

$$Na_2O + H_2O = 2NaOH$$
$$Na_2F_2 + 2HF = 2NaHF_2.$$

Hydrofluoric acid is a weak acid, that is to say, it is not highly dissociated. It is, however, stronger than such acids as acetic acid and nitrous acid, but weaker than phosphoric or sulphurous acids.

Hydrofluoric acid in solution reacts vigorously with the metals, forming fluorides, but the cold anhydrous acid does not attack most of the metals.

The action of hydrofluoric acid on silica and glass is of considerable interest. When strong hydrofluoric acid acts on silica, silicon fluoride is formed,

$$SiO_2 + 2HF \rightleftharpoons SiF_4 + 2H_2O.$$

If an excess of hydrogen fluoride is present, as when silica is immersed in the acid, the silicon fluoride does not escape but forms hydrofluosilicic acid,

$$SiF_4 + 2HF = H_2SiF_6.$$

The action on glass is similar. Ordinary glass may be regarded as $Na_2SiO_3 + CaSiO_3$. These react with the concentrated acid, giving sodium fluoride, calcium fluoride and silicon fluoride, but with solutions of the acid sodium and calcium silicofluorides result.

$$CaSiO_3 + 6HF = CaSiF_6 + 3H_2O.$$
$$Na_2SiO_3 + 6HF = Na_2SiF_6 + 3H_2O.$$

This effect of hydrogen fluoride on glass is utilised in glass etching. To engrave, say, the scale on a thermometer, it is coated with etching varnish [1] and the divisions are traced with a sharp point through the varnish. The scale is then placed in a deep vessel containing dilute

[1] A mixture of resin, turpentine and beeswax is satisfactory.

hydrofluoric acid, and after some time is removed and cleaned, when the markings will be deeply etched.

Opaque glass (frosted) is made by the action of the vapour of hydrogen fluoride or, much better, a solution of acid potassium fluoride in dilute hydrochloric acid.

The reaction is used as a test for fluorides. The suspected fluoride is gently warmed in a leaden dish together with a little sulphuric acid. A recognisable mark is scratched on a glass plate coated with beeswax, and the plate is placed on top of the dish. After some time the wax is cleaned off, and if fluorides were present the form of the mark scratched in the wax is visible. A very faint frosting is revealed by breathing on the plate.

The test described in § 602 may also be used, and is more convenient though less delicate.

**1035. The Fluorides.**—The fluorides of the metals resemble the chlorides. We may note as points of difference the ready formation of acid fluorides as $KHF_2$ and a general tendency to form double salts. Silver fluoride is soluble, while silver chloride is not ; calcium fluoride is not soluble, while calcium chloride is so.

**1036. Fluorine Oxides.**—Three of these are known, of formula $F_2O$, FO and $F_2O_2$. A gas containing some 70 per cent. of fluorine oxide is obtained by passing a stream of fine bubbles of fluorine through 2 per cent. sodium hydroxide solution,

$$2F_2 + 2NaOH = 2NaF + F_2O + H_2O.$$

This reaction with alkalis should be contrasted with that of chlorine, which forms a hypochlorite, NaOCl, and chloride, NaCl. No hypofluorites exist.

Fluorine oxide is a gas with an irritating fluorine-like odour. It is sparingly soluble in water and is not decomposed by water or glass. It slowly reacts with caustic potash, yielding oxygen,

$$F_2O + 2KOH = 2KF + O_2 + H_2O.$$

It is a very powerful oxidising agent.

*Difluorine dioxide* $F_2O_2$, has been prepared by the action of an electric discharge on a mixture of fluorine and oxygen at 15–20 mm. pressure and cooled by liquid air. It is a brown gas, which above −100° C. decomposes to a mixture of fluorine and oxygen.

**1037. The Fluorates.**—The electrolysis of a fused mixture of alkali hydroxide and fluoride yields a product from which fluorates are said to have been isolated. Silver fluorate, $AgFO_3$, has been described. They are powerful oxidising agents.

## CHLORINE Cl, 35·457

**1038. Historical.**—The element chlorine was first made by Scheele in 1774, by the reaction of hydrochloric acid and manganese dioxide.

He termed it *dephlogisticated marine acid air*, *i.e.*, hydrochloric acid from which the combustible principle, phlogiston (of which hydrogen was then believed largely to consist) had been removed. Later, when the phlogiston theory had been exploded, chlorine was for some time thought to be an oxygen compound, oxymuriatic acid; for it was believed that all acids contained oxygen, and, consequently, that chlorine, which with hydrogen made up hydrochloric acid, must contain oxygen also. This was doubted by Davy, who gave it its present name of chlorine,[1] and after his researches in 1810 it was generally accepted as an element.

**1039. Occurrence.**—The element does not occur free, but exists in enormous quantities as chlorides. These include *sodium chloride*, found as rock salt, and also in sea water; potassium chloride or *sylvine* and *potassium magnesium chloride* or *carnallite*, KCl, $MgCl_2$, $6H_2O$, found in the salt mines at Stassfurt.

**1040. Manufacture of Chlorine.**—Chlorine is manufactured at the present time by two chief methods:—

(1) Electrolytic methods.
(2) The oxidation of hydrogen chloride.

**1041. Electrolytic Chlorine.**—The electrolysis of sodium chloride solution yields considerably more than half the world's chlorine. The products of the electrolysis are caustic soda and chlorine, and the methods are fully discussed in § 230 (*q.v.*).

The chlorine so obtained is freed from moisture by drying with sulphuric acid, and is then very pure. It is either used on the spot for the manufacture of bleaching powder, etc., or is liquefied by pressure. The handling of chlorine in a compression pump is difficult owing to its corrosive action on cylinders and pistons. The difficulty is overcome by using a column of sulphuric acid as the piston. The liquid may be stored in steel cylinders, which are not attacked by the dry gas. It is even transported for long distances in steel boilers mounted on wheels.

**1042. Weldon Process.**—The action of manganese dioxide on hydrochloric acid is still used, though to a decreasing extent, to manufacture chlorine. Crude native manganese dioxide, *pyrolusite*, which is mined in Spain and other countries, is employed. The reaction, further discussed in § 1044, of this substance with hydrochloric acid produces manganous chloride and chlorine,

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The manganous chloride is reconverted in the Weldon process to manganese dioxide, which is then used again and again.

[1] Χλωρός—greenish yellow.

Hydrochloric acid is placed in a tank constructed of granite, and the manganese dioxide, which is recovered in the form of a thin mud, is allowed to flow in. Chlorine comes off and is carried by pipes to the place where it is required. The action is completed by blowing steam into the liquid. The solution of manganese chloride is then mixed with lime in tall iron cylindrical tanks. Air is blown through the warm mixture for some hours until the solid in suspension is fully oxidised. It is then allowed to settle out and when required is used to produce more chlorine.

The reactions concerned in the recovery are probably—

$$\text{(i.)} \quad MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2$$

$$\text{(ii.)} \quad Mn(OH)_2 + Ca(OH)_2 + O = \underset{\text{Calcium manganite.}}{CaO \,.\, MnO_2} + 2H_2O.$$

The last reaction does not appear to be as simple as the equation would indicate, for the resultant mud varies in composition between $CaO \,.\, MnO_2$ and $CaO \,.\, 2MnO_2$, and it is probable that the so-called manganite is a mixture of the hydroxides.

**1043. The Deacon Process.**—This process produces a much diluted chlorine very cheaply. If a mixture of air and hydrogen chloride at 400°–450° C. is led over a suitable catalyst, which is usually cupric chloride, $CuCl_2$, chlorine and water are produced.

$$4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2 - 14{,}700 \text{ cals.}$$

Hydrogen chloride, which must be fairly pure, is mixed with air, heated to *c.* 220° C., and led into vertical cylinders packed with porous earthenware balls impregnated with cupric chloride. About 60 per cent. of the hydrogen chloride is converted into chlorine; the remainder is dissolved out of the gas in the manner described in § 1052. The chlorine obtained is mixed with about 90 per cent. of nitrogen and is not pure enough for liquefaction. It can, however, be used for the manufacture of bleaching powder in special types of chamber. The process is a rather difficult one to maintain at full efficiency, but owing to the cheapness of the materials it holds its own—particularly on the Continent.

**1044. Laboratory Preparation of Chlorine.**—Chlorine is usually prepared in the laboratory by the oxidation

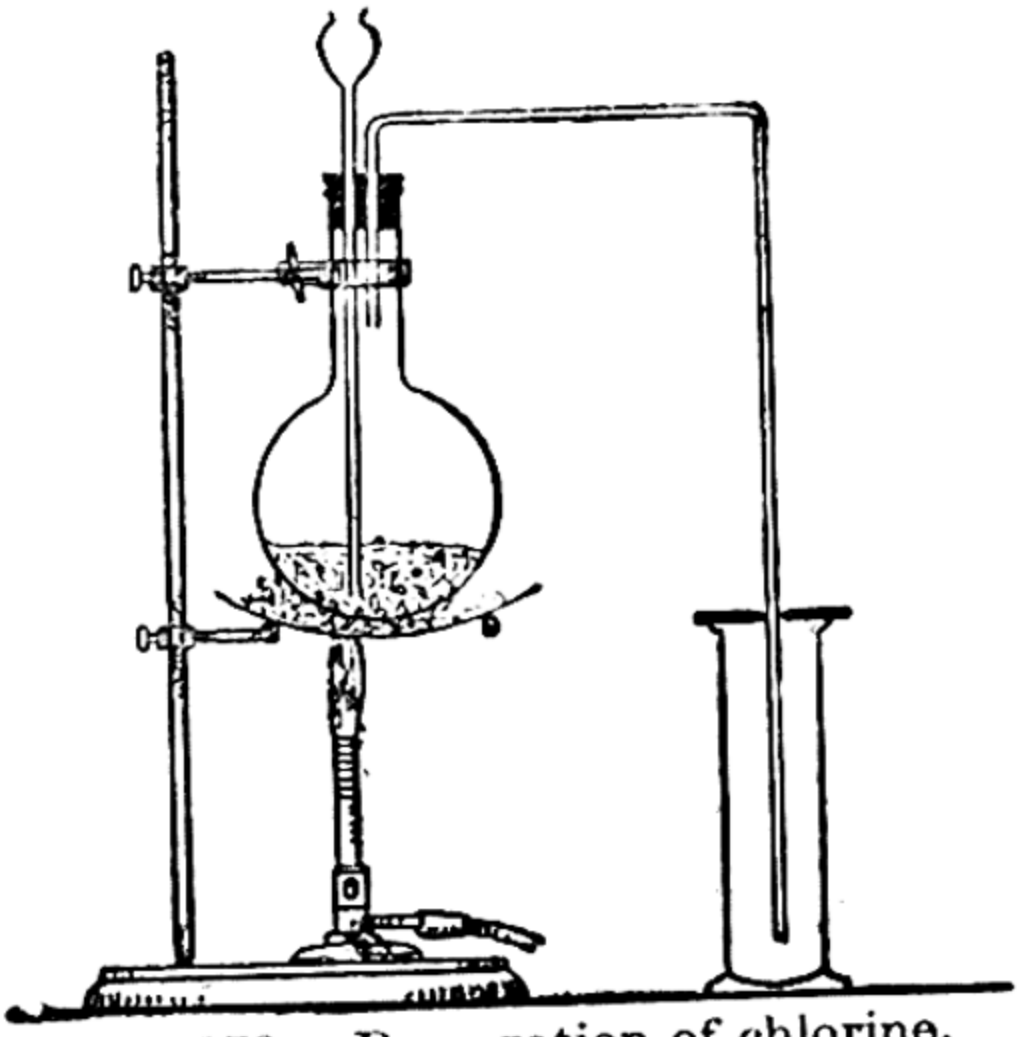


FIG. 173.—Preparation of chlorine.

of hydrochloric acid. As oxidising agents manganese dioxide or potassium permanganate are used, though several other oxidising agents, such as lead dioxide and nitric acid, are available.

(1) To prepare considerable quantities of chlorine in the laboratory it is best to cover manganese dioxide, preferably in lumps, with hydrochloric acid, and heat gently on a sand-bath. The apparatus of Fig. 173 is suitable. The complete reaction is

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2,$$

but it certainly takes place in two stages. It is probable that manganese tetrachloride is formed and at once begins to decompose, even in the cold, into manganese trichloride and chlorine,

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O$$

$$2MnCl_4 = 2MnCl_3 + Cl_2,$$

while the manganese trichloride itself decomposes when heated into manganese dichloride and chlorine,

$$2MnCl_3 \rightleftharpoons 2MnCl_2 + Cl_2.$$

The gas so prepared contains hydrogen chloride and moisture. It should be washed with a little water and then dried with sulphuric acid. It may be collected by downward displacement or over hot water, but not over cold water, in which it dissolves rather readily, nor over mercury, with which it reacts.

A mixture of common salt, manganese dioxide and sulphuric acid is often used in place of hydrochloric acid and manganese dioxide,

$$2NaCl + MnO_2 + 3H_2SO_4 = 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2.$$

(2) The action of potassium permanganate on concentrated hydrochloric acid yields the gas without heating. The former substance is now so cheap that the method is very convenient. The potassium permanganate may be placed in a flask and concentrated hydrochloric acid allowed to drop on to it from a tap funnel. Towards the close of the experiment the liquid may be warmed to decompose the manganese trichloride formed. The gas is washed and dried as in method (1),

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

(3) An excellent practical method of preparing chlorine is by the action of an acid upon bleaching powder (*q.v.*, § 1066). The apparatus shown in Fig. 177 may be employed.

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2.$$

Compressed blocks of bleaching powder, which may be used in a Kipp's apparatus, are now sold.

(4) The action of hydrochloric acid upon red lead, lead peroxide,

or potassium dichromate is occasionally used for the preparation of the gas,

$$Pb_3O_4 + 8HCl = 3PbCl_2 + 4H_2O + Cl_2$$
$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$$
$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

(5) The electrolysis of hydrochloric acid yields chlorine. The apparatus of Fig. 155, which should be fitted with *carbon* poles, may be used. Little chlorine is evolved until the acid becomes saturated,

$$2HCl = H_2 + Cl_2.$$

The electrolysis of solutions of chlorides is the most important process for manufacturing chlorine.

(6) Certain chlorides, notably magnesium chloride, decompose when heated in air.

$$2MgCl_2 + O_2 = 2MgO + 2Cl_2$$

This reaction has been practically utilised.

(7) The chlorides of gold and platinum decompose when heated to about 200° C.,

$$2AuCl_3 = 2Au + 3Cl_2.$$

(8) A mixture of hydrochloric acid (4 parts) with nitric acid (1 part) forms *aqua regia*. This liquid, when heated, evolves chlorine and nitrosyl chloride, and consequently will attack many substances not attacked by other acids, *e.g.*, gold, platinum, certain metallic sulphides. The equation has been given as

$$3HCl + HNO_3 = 2H_2O + NOCl + Cl_2,$$

but is doubtless more complex.

(9) Hydrogen chloride may be oxidised by air in presence of a suitable catalyst. The Deacon process, described in § 1043, passes a mixture of hydrogen chloride and air over a catalyst consisting of a copper salt.

The reactions are probably

$$2CuCl_2 = Cu_2Cl_2 + Cl_2$$
$$Cu_2Cl_2 + O = Cu_2OCl_2$$
$$\underline{Cu_2OCl_2 + 2HCl = H_2O + 2CuCl_2}$$
$$2HCl + O = H_2O + Cl_2$$

though doubt has been cast on this explanation of the process.

**1045. Formula and Atomic Weight.**—The atomic weight of chlorine has been determined by the very accurate researches of Richards described in § 70. That the atomic weight was approximately 35·5 was shown by evidence drawn from the vapour densities of its compounds. The densities of its volatile compounds (chlorine, hydrogen chloride, chlorine peroxide, many volatile chlorides, and organic chlorinated compounds) show that one gram-molecular

weight of the compound never contains less than 35·45 gms. of chlorine. The figure is taken to show that chlorine has an atomic weight equal to its equivalent weight—35·457 ; and this is confirmed by its position in the Periodic table and the use of the mass spectrograph (§ 149). The density of chlorine gas is 35·5 ($H_2 = 1$). Its molecular weight is 71, and its formula is $Cl_2$.

It had been long thought remarkable that of all the elements of the first two short periods of the Periodic table, Li to Cl, the latter was the only one which had an atomic weight not approximating to a whole number. The use of the mass spectrograph shows that chlorine is a mixture of isotopes of atomic weights 37 and 35. Attempts have been made to separate these isotopes by diffusion. When the gas is allowed to diffuse through a fine hole or a porous plug the lighter isotope should pass through faster than the heavier in the ratio of $\sqrt{37} : \sqrt{35}$, *i.e.*, as 1,003 : 1,000. This difference in the rate of diffusion is so small that it is difficult to effect any considerable separation, though fractions of chlorine differing in atomic weight by 1 part in 8,000 have been obtained. The fractional diffusion of hydrogen chloride has proved more effective, for by fractionally diffusing the gas through porous pipe stems a specimen yielding chlorine of atomic weight 35·418 has been obtained. The thermal diffusion method is still more effective and hydrogen chloride containing 40 per cent. of $HCl^{37}$ instead of the usual 23 per cent. has been made.

**1046. Properties of Chlorine.**—Chlorine is a greenish-yellow gas with a very characteristic smell—pungent and suffocating. Even when highly diluted with air (*c.* 1 : 50,000), it causes serious injury to the lungs when breathed. It was used as a poison gas in the war of 1914–1918, being well adapted to this purpose by its high density, its cheapness and its poisonous qualities. Care is required in its use in the laboratory, and operations involving its use should be conducted in a good fume cupboard or the open air. It has a strong antiseptic action and forms a valuable disinfectant, its properties in this regard being probably due to the hypochlorous acid (*q.v.*), which it forms in contact with moisture. It is used for the large-scale sterilisation of drinking water. The density of the gas (35·46, $H_2 = 1$ ; 2·46, air = 1) is the highest of those of the common gases, Chlorine is readily liquefied by compression or by cooling to a dark greenish-yellow liquid, which boils at — 33·6° C. It is commonly sold as a liquid stored under pressure in steel cylinders. These are not attacked by dry chlorine.

Chlorine gas is soluble in water, 1 volume of water dissolving 2·37 volumes at 10° C., 3·04 at 0° C. Chlorine water, as the solution is called, has the smell, colour and taste of the gas. The chemical

reactions between chlorine and water are discussed below. Chlorine readily dissolves in carbon tetrachloride, and the solution finds considerable use as a reagent.

**1047. Chemical Properties.**—Chlorine is highly reactive, being only less so than fluorine. Among the non-metallic elements, oxygen, nitrogen and carbon do not react directly with chlorine, but hydrogen, boron, silicon, phosphorus, arsenic, sulphur, selenium, tellurium, fluorine, bromine, and iodine all react directly, forming the chlorides.

Sulphur, phosphorus and arsenic burn vigorously in the gas. The particular reactions are to be found under the headings of the elements in question.

The reaction between hydrogen and chlorine is of particular interest and is quite complicated in character. If a mixture of equal volumes of hydrogen and chlorine be allowed to remain in the dark no reaction occurs in the cold. If heated the gases explode, forming hydrogen chloride,

$$H_2 + Cl_2 = 2HCl.$$

If, however, the cold mixture of hydrogen and chlorine is exposed to a bright light, *e.g.*, that of the sun or of burning magnesium, they combine explosively.

If the gases are placed in diffused light, such as that of an ordinary room, the effect is very interesting. No combination takes place for some hours, and then the gases begin to react and continue to do so until no chlorine remains. This *induction period*, when no reaction occurs, has been shown to be due to the presence of a negative catalyst or inhibitor, probably nitrogen chloride $NCl_3$, formed by the action of the chlorine upon traces of ammonia or nitrogen compounds contained in the water with which it has come into contact. This nitrogen chloride is destroyed by light, and until it has disappeared no reaction takes place. The rate of the reaction has been studied, and it is found that a quantum of light causes about half a million molecules to react. The reaction is evidently of the chain type. It has recently been shown that atomic chlorine brings about the reaction (§ 1049a), and it has also been shown that the presence of moisture is not essential. These newly discovered facts support the theory originally suggested by Nernst that the light energy breaks up a chlorine molecule,

$$Cl_2 + h\nu = Cl + Cl,$$
quantum of light.

and that the following series of reactions then repeats itself until it is brought to a stop,

$$(1)\ H_2 + Cl = HCl + H$$
$$(2)\ H + Cl_2 = HCl + Cl$$

say by the chlorine or hydrogen atoms recombining or meeting something reactive.

Oxygen decreases the speed of the reaction because it breaks the chains by combining with H to form OH and finally $H_2O$.

Chlorine can be *activated* by exposure to ultra-violet light and then reacts

with benzene in the dark and with sulphur in the cold. It is stated that a small decrease of volume occurs, and this may be due to the formation of $Cl_3$ molecules.

The metals are all attacked by chlorine, and some, such as antimony, copper, tin, lead, iron, the alkali and alkaline earth metals, zinc and magnesium, burn in the gas. Where two chlorides exist the higher is usually formed,

$$2Fe + 3Cl_2 = 2FeCl_3$$
$$Cu + Cl_2 = CuCl_2,$$

unless it is markedly unstable. Dry chlorine is much less reactive than the moist gas (§ 205).

Chlorine reacts with water. A solution of chlorine water contains hypochlorous acid,

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl,$$

and hydrochloric acid in small quantity. When exposed to light the hypochlorous acid decomposes,

$$2HClO = 2HCl + O_2,$$

and so chlorine water on standing in the light is gradually converted into hydrochloric acid and oxygen,

$$2Cl_2 + 2H_2O = 4HCl + O_2.$$

On cooling chlorine water to 0° C. pale yellow crystals of chlorine hydrate deposit. These have a formula which does not appear to be clearly known. Formulæ between $Cl_2 . 4H_2O$ and $Cl_2 . 12H_2O$ have been given and $Cl_2 . 6H_2O$ appears to be the most likely.

Gentle warming decomposes the hydrate and liberates chlorine. The original liquefaction of chlorine by Faraday was performed by placing chlorine hydrate crystals in one end of a strong right angled glass tube and cooling the other end with ice and salt. The chlorine hydrate crystals liberated about a hundred times their volume of chlorine, which, accumulating under high pressure in the tube, condensed as an oil in the cold end.

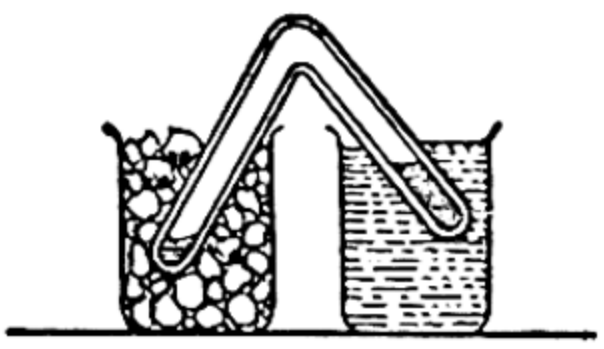


Fig. 174.—Preparation of liquid chlorine from chlorine hydrate.

It is related that Dr. Paris, entering the laboratory, took Faraday, a younger man, to task for using oily and dirty apparatus. When the pressure was released the apparent oil disappeared in the form of chlorine gas, and Faraday had the pleasure of telling Paris that the 'oil' he had noticed was the hitherto unknown liquid chlorine. Chlorine is now liquefied by pumping it into cylinders under pressure (§ 1041).

The hydrides of the non-metals in general react with chlorine, giving hydrogen chloride and the element which may or may not itself react with chlorine to form its chloride.

Thus hydrogen sulphide yields hydrogen chloride and sulphur, which latter may react to form sulphur chloride,

$$H_2S + Cl_2 = 2HCl + S$$
$$2S + Cl_2 = S_2Cl_2.$$

Ammonia yields nitrogen,

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

The numerous hydrides of carbon react in three different ways with chlorine.

Saturated hydrocarbons mixed with chlorine and exposed to light form *substitution products* (see p. 422).

$$CH_4 + Cl_2 = CH_3Cl + HCl,$$

in which one or more atoms of chlorine *take the place of* a corresponding number of atoms of hydrogen.

Unsaturated hydrocarbons *add on* chlorine and form saturated compounds. Thus

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + Cl_2 = \begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix}$$

ethylene and chlorine form dichlorethane (ethylene chloride).

Finally, any hydrocarbon, if ignited, will *burn* in chlorine, forming hydrogen chloride and carbon,

$$C_6H_6 + 3Cl_2 = 6C + 6HCl,$$

a red and very smoky flame being produced. Some hydrocarbons, such as turpentine, ignite spontaneously.

Chlorine displaces bromine and iodine from their compounds with metals,

$$Cl_2 + 2KBr = 2KCl + Br_2.$$

**1048. Oxidation and Reduction—Chlorine as oxidising agent.**

A substance is said to be *oxidised* when

(1) It adds on oxygen, chlorine or other atoms or groups capable of forming electronegative radicals or anions.

(2) It loses hydrogen, metal, or electropositive radicals or cations.

(3) It loses electrons.

A substance is said to be *reduced* when

(1) It loses oxygen, chlorine, or other atoms or groups capable of forming electronegative radicals or anions.

(2) It gains hydrogen, metal or electropositive radicals or cations.

(3) It gains electrons.

*An oxidising agent* is one which is capable of causing substances to be oxidised and is therefore able to impart to them oxygen, chlorine, electronegative radicals, etc., to remove hydrogen or metal or electrons from them.

*A reducing agent* is one which is capable of causing substances to be reduced by removing from them oxygen, chlorine, electronegative radicals, etc., or by imparting hydrogen or metal or electrons to them.

Chlorine is an oxidising agent and can act in almost all the ways mentioned in the definition. Thus :—

(1) *a. Oxygen imparted to another substance.*

Chlorine in presence of water adds oxygen to many substances : thus sulphites are oxidised to sulphates,

$$Na_2SO_3 + H_2O + Cl_2 = Na_2SO_4 + 2HCl.$$

(1) *b. Chlorine imparted to another substance.*

Ferrous chloride is oxidised to ferric chloride,

$$2FeCl_2 + Cl_2 = 2FeCl_3.$$

(1) *c. Acid radical imparted to another substance.*

Ferrous sulphate oxidised to ferric sulphate,

$$2FeSO_4 + H_2SO_4 + Cl_2 = Fe_2(SO_4)_3 + 2HCl.$$

(2) *Hydrogen taken from a substance.*

Hydrogen sulphide is oxidised to sulphur,

$$H_2S + Cl_2 = S + 2HCl.$$

(3) *Electrons taken from a substance.*

Iodide ion oxidised to iodine,

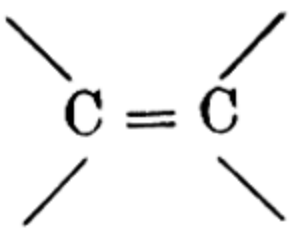
$$2I^- + Cl_2 = I_2 + 2Cl^-$$

Stannous ion oxidised to stannic ion,

$$Sn^{++} + Cl_2 = Sn^{++++} + 2Cl^-$$

Every oxidation involves a reduction. Thus sulphites, ferrous salts, hydrogen sulphide, iodides, stannous compounds are all reducing agents and reduce the chlorine to hydrogen chloride, a chloride, or generally chloride ion.

**1049. Bleaching Action of Chlorine.**—Chlorine bleaches many organic colouring matters. Colouring matters are usually fairly unstable compounds, the colour of which often depends on a system of atoms containing double bonds,



Chlorine oxidises such compounds readily. The gas only reacts in presence of moisture. It is chiefly used in the bleaching of cellulose (cotton and linen), which is unharmed by the gas; wool and silk, which are nitrogenous compounds, containing the $-NH_2$ grouping, are damaged, and are therefore bleached with sulphur dioxide. The usual method of bleaching is to pass the goods through a solution of bleaching powder, $CaOCl_2$, and then through a weak acid bath, Chlorine is formed within the fibre itself, and so bleaches it (§ 1066*a*).

$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

The method avoids the danger of handling gaseous chlorine.

The bleaching of sulphur dioxide by *reduction* (*q.v.*) is in sharp contrast to the action of chlorine by *oxidation*.

**1049a. Atomic Chlorine, Cl.**—By subjecting chlorine to an electrodeless discharge (25,000 volts) a slight expansion occurs due to the formation of some 0·2 per cent. of atomic chlorine. This is highly reactive. Unlike dry molecular chlorine, it reacts with silver and other metals in the cold. It reacts with hydrogen even in the dark, and the reaction, *once started by the small proportion of atomic chlorine*, will continue until much of or all the molecular chlorine has reacted. This is strong evidence for the Nernst chain theory of the reaction of hydrogen and chlorine.

**1050. Detection of Chlorine.**—Traces of chlorine are readily detected by their action on potassium iodide. Papers dipped in a mixture of solutions of potassium iodide and starch turn blue when traces of chlorine act upon them, liberating iodine,

$$Cl_2 + 2KI = 2KCl + I_2.$$

Many other oxidising agents also liberate iodine. In larger quantity chlorine is detected by its action upon moist litmus paper, which is quickly bleached.

Free chlorine is determined by passing it into an excess of potassium iodide solution and titrating the liberated iodine with sodium thiosulphate (§ 1090).

## HYDROGEN CHLORIDE

**1051. Hydrogen Chloride, Hydrochloric Acid, HCl.**—The knowledge of the solution of hydrogen chloride in water, which was obtained by distilling sulphates with salt dates from the time of the Latin works attributed to Geber (*c.* 1100).

The gas hydrogen chloride has been known since the year 1727, when Stephen Hales noticed the production of a gas from sulphuric

acid and salt. Priestley rediscovered the gas in 1772 and termed it *marine acid air*. When Lavoisier's oxygen theory of acids was in vogue the name muriatic acid was given it. Later it was recognised as a compound of the elements hydrogen and chlorine and was termed hydrochloric acid.

*Occurrence.*—Hydrogen chloride is occasionally found in the gases emitted from volcanoes.

**1052. Manufacture.**—Hydrogen chloride is manufactured as a by-product in the manufacture of 'salt-cake' sodium sulphate (§ 235). The process has become less widely used now that the Leblanc process for the manufacture of soda has been displaced by the ammonia-soda and electrolytic processes. Common salt is placed in a shallow pan of thick iron, gently heated from below by flue gases,

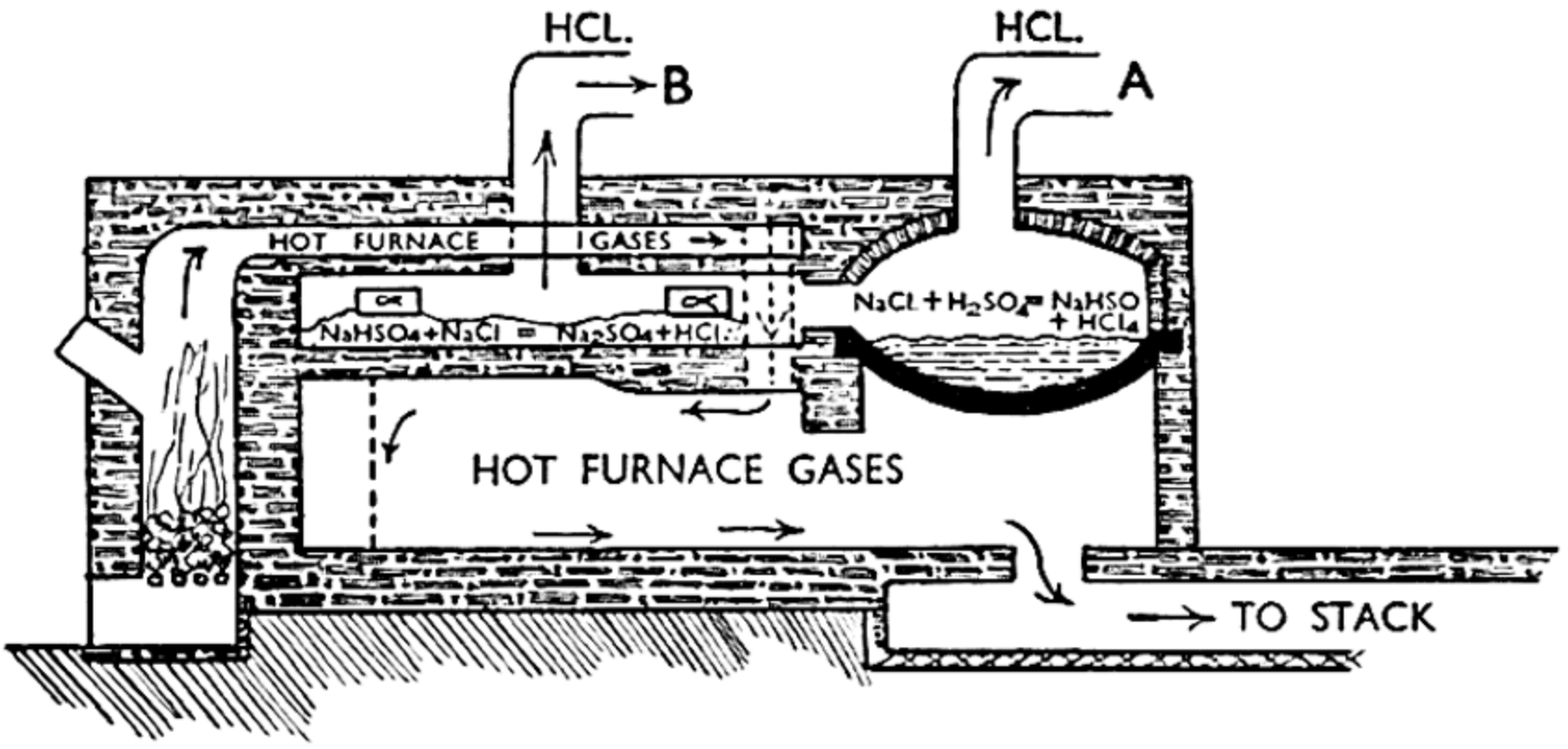



FIG. 175.—Manufacture of hydrogen chloride.

and sufficient sulphuric acid to convert it into normal sodium sulphate is run on to it from a pipe not shown in the figure. At the temperature of the pan there occurs only the reaction to the acid sulphate $NaHSO_4$

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

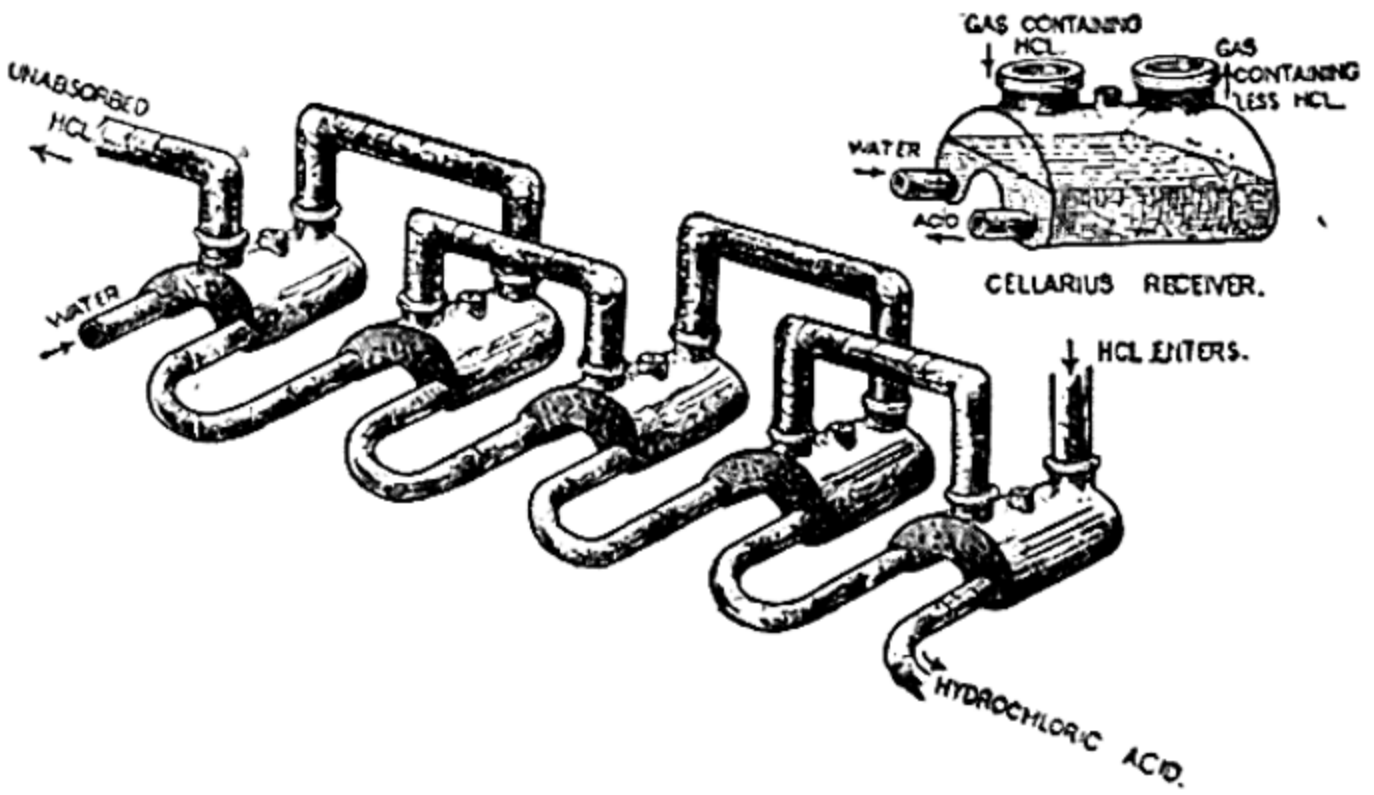



FIG. 176.—Absorption of hydrogen chloride.

The hydrogen chloride is led off by the pipe A and dissolved in water as described below. The mixture of common salt and sodium hydrogen sulphate is then raked out into a muffle, above and below which circulate the hot gases from a small furnace. Here, at about 500° C., a further reaction takes place and more hydrogen chloride is evolved, normal sodium sulphate being formed,

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

The gas escapes through the pipe B.

The gases are led up towers of siliceous sandstone, packed with coke, over which water flows, and dissolve forming hydrochloric acid. Alternatively they may be led through a series of from twenty to sixty receivers, the Cellarius type illustrated being one of the best. Water flows in at one end and hydrogen chloride gas at the other. The water absorbs the gas and leaves the apparatus as concentrated hydrochloric acid. The fresh water comes in at the far end and so exerts its full solvent powers on the nearly exhausted gas, while the concentrated acid before passing out meets with the undiluted gas and becomes still further concentrated.

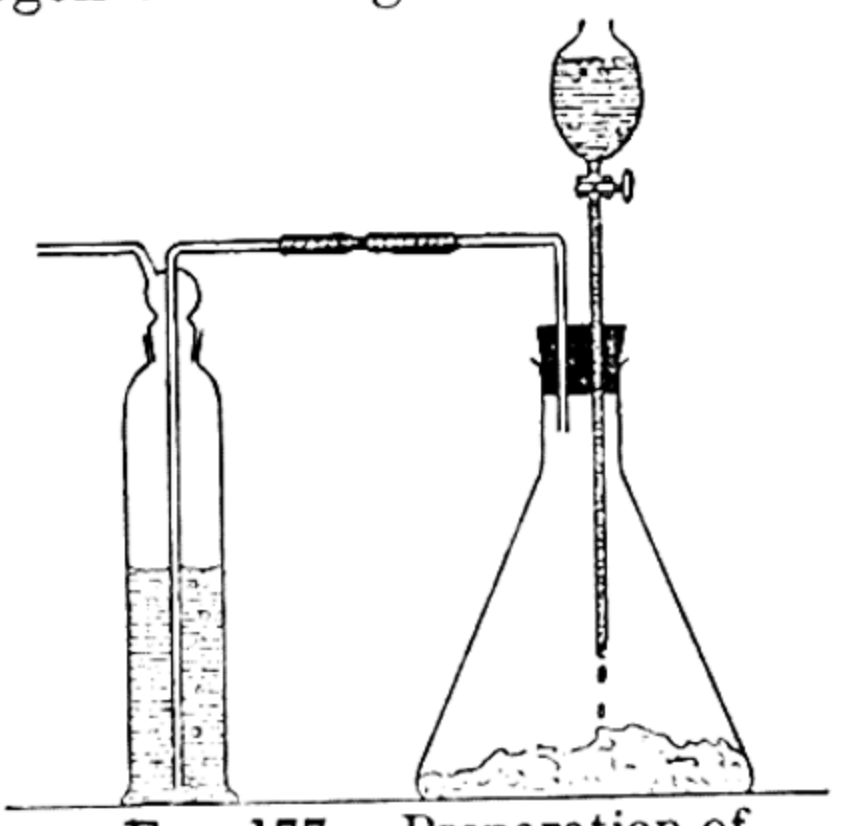


FIG. 177.—Preparation of hydrogen chloride.

Commercial hydrochloric acid contains some 32 per cent. of hydrogen chloride.

The manufacture of the acid by the direct combination of electrolytic chlorine and hydrogen is now much in use. The chlorine is burned in an atmosphere of hydrogen, silica-ware burners being employed. The resulting gases are absorbed as described above. The resulting acid is of very high purity.

**1053. Laboratory Preparations.**—(1) Hydrogen chloride is ordinarily made by the action of concentrated sulphuric acid on common salt. Other chlorides may be used in place of common salt. The reaction at temperatures below a red heat is such that the acid sulphate of sodium is formed,

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

The apparatus figured is convenient. The gas obtained by dropping concentrated sulphuric acid on well dried common salt is practically dry and pure, but may be dried over concentrated sulphuric acid if necessary, and collected over mercury or by displacement. Collection over water is impossible, as the gas is very soluble.

If a prolonged steady stream of the gas is required, *e.g.*, for

saturating a liquid with hydrogen chloride, lumps of crystallised ammonium chloride should be used in place of common salt.

(2) A useful practical method is the action of concentrated sulphuric acid on concentrated hydrochloric acid. The sulphuric acid is allowed to flow from a tube (bent as in the illustration) into concentrated hydrochloric acid. The form of tube illustrated ensures adequate mixing of the acids and enables a steady stream of gas to be obtained. The hydrogen chloride is evolved and is dried and collected as described above.

*Other Methods.*

(3) The reaction between hydrogen and chlorine (*v.* § 1047) yields hydrogen chloride. The reaction is of explosive violence. It is, however, used on the commercial scale, where electrolytic chlorine is cheap.

(4) The reaction of chlorine with many hydrogen compounds yields hydrogen chloride (*v.* § 1047).

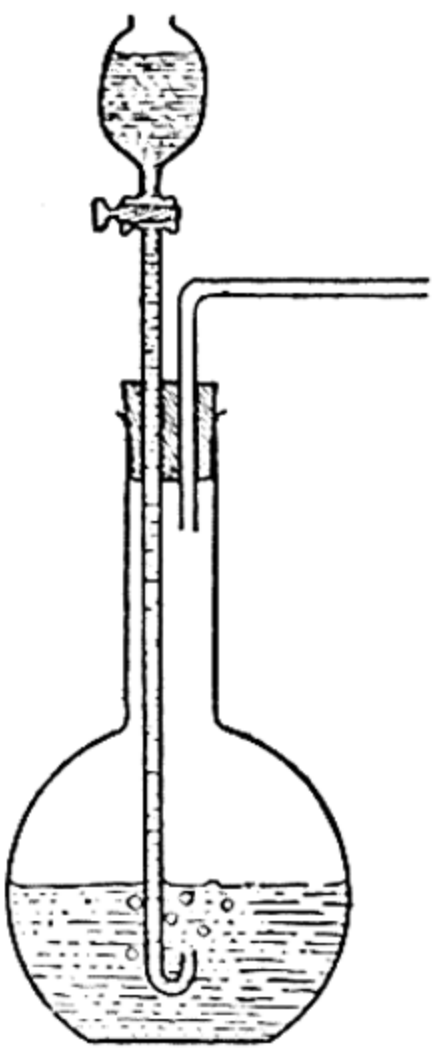


FIG. 178.—Preparation of hydrogen chloride.

(5) The reaction of water with such chlorides as contain chlorine united with a non-metal, metalloid, or electronegative atom or group of atoms, usually liberates hydrochloric acid. Among such reactions we may number (*a*) the reaction of water with the chlorides of all the non-metals except those of carbon,

$$PCl_3 + 3H_2O = P(OH)_3 + 3HCl.$$

(*b*) The reaction of water with the chlorides of antimony and aluminium and tetravalent tin,

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

(*c*) The reaction of water with acid chlorides such as phosphoryl, sulphuryl and carbonyl chlorides,

$$POCl_3 + 3H_2O = PO(OH)_3 + 3HCl.$$

**1054. Formula and Molecular Weight.**—These matters are fully discussed in § 48, being fundamental in the study of molecular and atomic weights.

**1055. Physical Properties.**—Hydrogen chloride is a colourless gas which fumes in air. The fuming is due to the fact that a solution of hydrogen chloride is less volatile than water, and consequently a mixture of water vapour and hydrogen chloride will condense to droplets of hydrochloric acid. It has an irritating smell and, in solution, an acid taste. The gas is poisonous, but much less so than chlorine. The concentrated solution in water is also poisonous in

view of its intense corrosive action on the mouth and throat. The dilute acid is harmless and, indeed, some 0·4 per cent. is regularly present in the gastric juice secreted by the stomach. Hydrogen chloride is heavier than air (sp. gr. 18·23, $H_2 = 1$ ; 1·26, air = 1). It is liquefied by cold and pressure to a colourless liquid boiling at −85° C.

Hydrogen chloride is very soluble in water. One volume of water at 0° C. dissolves 525 volumes of hydrogen chloride. The solution is known as hydrochloric acid (spirits of salt). The acid commonly sold has sp. gr. 1·16 and contains 32 per cent. of hydrogen chloride corresponding to a solution of about 237 vols. of hydrogen chloride at 15° C. in 1 volume of water. A stronger solution (sp. gr., 1·200) is sold as fuming hydrochloric acid and contains up to 39·1 per cent. of the gas.

The solutions of hydrogen chloride are colourless liquids which, if they contain more than 20 per cent. of hydrogen chloride, fume in moist air.

When strong solutions of the acid are heated the vapour contains a greater proportion of hydrogen chloride and a less proportion of water than the original solution. The solution thus becomes weaker. The vapour from weak solutions, on the other hand, contains a greater proportion of water and a less proportion of hydrogen chloride than the solution itself. Consequently these solutions become stronger. A solution containing 20·24 per cent. of hydrogen chloride at atmospheric pressure gives off a vapour also containing 20·24 per cent. of hydrogen chloride. Thus this solution, when evaporated, does not change in composition, and consequently its boiling point does not alter. It therefore follows that any solution of hydrochloric acid when heated gives off either water or hydrogen chloride until it contains 20·24 per cent. of the latter, when no further change takes place. This *constant boiling mixture* has the highest boiling point of any, in this case 110° C. This must necessarily be so, for any mixture which does not give off vapour of the same composition as itself will give off its most volatile portion and its boiling point will *rise* until it reaches the composition of the constant boiling mixture. Sulphuric acid, nitric acid, and the other halogen hydrides form such constant boiling mixtures.

The composition of the constant boiling mixture varies slightly with the pressure. This shows that it cannot be a compound despite its apparently constant composition.

Hydrochloric acid is one of the four strongest acids, which are completely dissociated in solution. The others are hydrobromic acid, hydriodic acid and perchloric acid.

**1056. Chemical Properties.**—Hydrogen chloride does not burn in

the usual sense. It reacts with free oxygen in presence of certain catalysts, such as copper salts, forming water and chlorine (*v.* § 1043)

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

It does not react with any of the other non-metals, except fluorine, which displaces the chlorine,

$$2HCl + F_2 = H_2F_2 + Cl_2.$$

Hydrogen chloride reacts with the metals in a manner typical of an acid. When in the form of a gas, it reacts with the metals when they are heated ; in solution in water it attacks most of them in the cold. All the metals are attacked except gold, silver, mercury and the platinum metals. Copper is attacked only in presence of air. The *lower* chloride is usually formed together with hydrogen,

$$Fe + 2HCl = FeCl_2 + H_2.$$

or

$$Fe + 2H^+ = Fe^{++} + H_2.$$

The solution exhibits the usual properties of a strong acid. It reacts with the oxides and hydroxides of metals, forming the corresponding chlorides and water.

Hydrochloric acid displaces most weak acids from their salts (cf. § 164). Thus carbonates, sulphides, sulphites, etc., are decomposed, and the gaseous acid or acidic oxide is produced,

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 \uparrow + H_2O.$$

If the acid is non-volatile it will be formed and may, if slightly soluble, be precipitated, especially as the solubility of acids in a solution containing much free acid is slight (§ 118). Thus hydrochloric acid precipitates boric, silicic and many organic acids from their salts.

If the acid is neither volatile nor sparingly soluble it will be formed but will not be able to be isolated. Thus, when sulphates or phosphates are mixed with hydrochloric acid some sulphuric and phosphoric acid are undoubtedly formed, but cannot be isolated,

$$Na_2SO_4 + 2HCl \rightleftharpoons 2NaCl + H_2SO_4.$$

Hydrochloric acid reacts with the stronger oxidising agents to form chlorine, the general equation being

$$2HCl + (O) = H_2O + Cl_2.$$

Among the oxidising agents which will oxidise hydrochloric acid are the dioxides of manganese and lead, the chromates, dichromates, permanganates, perchlorates, chlorates, nitrates. Most of these reactions are discussed in § 1044 in connection with the preparation of chlorine.

**1057. The Chlorides of the Metals.**—The chlorides of each particular metal are discussed under the heading of that metal; but a general survey of their properties may be of value.

The chlorides are usually well crystallised and are freely soluble in water with the exception of the chlorides of univalent heavy metals ($Hg_2Cl_2$, $Cu_2Cl_2$, AgCl, TlCl, AuCl). Lead chloride and palladous chloride are sparingly soluble. Their solubility is as a rule much diminished by the presence of hydrochloric acid (*v.* § 118). They are the most volatile of the metallic salts and may often be sublimed.

The chlorides of the metals, other than gold and platinum, are not decomposed by heat. Some of them react with water, forming oxychlorides. This is particularly the case with the metals with metalloid characteristics—tin, antimony and bismuth.

With the exception of mercuric chloride they all react with sulphuric acid, giving sulphates and hydrogen chloride,

$$CuCl_2 + H_2SO_4 = CuSO_4 + 2HCl,$$

though the reaction between the very insoluble silver chloride and sulphuric acid is almost inappreciable. Nitric acid oxidises them, and repeated heating with nitric acid converts them into nitrates,

$$ZnCl_2 + 2HNO_3 \rightleftharpoons Zn(NO_3)_2 + 2HCl$$
$$3HCl + HNO_3 = 2H_2O + NOCl\uparrow + Cl_2\uparrow.$$

Other acids do not affect them. The reaction which is characteristic of the chloride ion, and therefore a useful test for hydrochloric acid and chlorides, is the formation of silver chloride.

**1058. Tests for Chlorides.**—The suspected chloride is dissolved in water and an equal volume of dilute nitric acid is added. If, on addition of silver nitrate solution, a white precipitate is produced which gathers on shaking into curds or flocks, which is soluble in ammonia and is reprecipitated by nitric acid and which turns blue in the light—a chloride is present,

$$Ag^+ + Cl^- \rightleftharpoons AgCl.$$

Bromides give a cream-coloured precipitate and iodides a pale yellow one. Neither of these turn blue in the light.

A second useful test, particularly applicable to solids, is to mix them with an equal volume of manganese dioxide and warm with concentrated sulphuric acid. If chlorine is evolved, detected by its bleaching action on litmus, a chloride was present (see § 1044 (1)).

An interesting test consists of mixing the substance with potassium dichromate and sulphuric acid. On warming, red vapours of

chromyl chloride (§ 993) are evolved,

$$K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl = 2KHSO_4 + 3H_2O + \\ + 2CrO_2Cl_2 + 4NaHSO_4.$$

These may be distinguished from bromine or nitrogen peroxide by passing them into caustic soda solution, when a *yellow* solution of chromate results. The test serves to detect chloride in presence of much bromide or iodide (*v.* § 993).

**1059. Oxides of Chlorine.**—Chlorine forms six oxides, of which only chlorine dioxide is at all commonly met with :—

| | |
|---|---|
| Chlorine monoxide . . . . . | $Cl_2O$ |
| Chlorine dioxide . . . . . | $ClO_2$ |
| Chlorine trioxide . . . . . | $ClO_3$ |
| Chlorine hexoxide . . . . . | $Cl_2O_6$ |
| Chlorine heptoxide . . . . . | $Cl_2O_7$ |
| Chloride tetroxide . . . . . | $(ClO_4)_x$ |

The nomenclature is rather unsystematic.

All these oxides are very unstable substances and highly explosive.

Chlorine sesquioxide $Cl_2O_3$ has been described but appears to be a mixture of chlorine and chlorine dioxide.

**1060. Chlorine Monoxide $Cl_2O$** is made by passing a slow current of dry chlorine over mercuric oxide contained in a tube kept cool by water,

$$2Cl_2 + HgO = HgCl_2 + Cl_2O.$$

The gas is condensed out by means of a freezing mixture.

It is a pale orange-yellow gas, which readily condenses to a liquid boiling at 3·8° C. When heated it explodes at quite low temperatures, forming chlorine and oxygen,

$$2Cl_2O = 2Cl_2 + O_2.$$

It combines with water, forming hypochlorous acid (§ 1064), and

$$Cl_2O + H_2O = 2HOCl$$

may therefore be regarded as hypochlorous anhydride.

**1061. Chlorine Dioxide $ClO_2$** is formed by the action of concentrated sulphuric acid on a chlorate. The chloric acid (§ 1069) formed decomposes into perchloric acid, chlorine dioxide and water,

$$KClO_3 + H_2SO_4 = KHSO_4 + HClO_3$$
$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O.$$

No attempt should be made to collect the gas or even to make it in anything larger than a test tube, for the heat of the reaction is usually enough to cause it to explode.

Chlorine dioxide is a brownish-green gas with an odour resembling, though distinct from, that of chlorine. It is liquefied when cooled to 0° C., forming a liquid boiling at 9° C.

The gas explodes when heated to about 50° C., forming chlorine and oxygen. It is an extremely powerful oxidising agent, causing most combustibles to burst into flame. Thus a mixture of starch, sugar, sawdust, etc., with potassium chlorate, ignites when a drop of sulphuric acid is let fall upon it.

Chlorine peroxide dissolves in water and probably forms chlorous and chloric acids,

$$H_2O + 2ClO_2 = HClO_2 + HClO_3.$$

Passed into solutions of alkalis, chlorites and chlorates are formed.

**1061a. Chlorine Trioxide and Hexoxide.**—The action of ozone on chlorine dioxide at 0° C. yields the gas chlorine trioxide $Cl_2O_6$. The latter can also be made by the action of light on chlorine dioxide. Its vapour contains the form $ClO_3$. Chlorine hexoxide is explosive. It soon breaks up at room temperature, giving chlorine dioxide, chlorine and oxygen. With water it gives chloric and perchloric acids,

$$Cl_2O_6 + H_2O = HClO_3 + HClO_4.$$

**1062. Chlorine Heptoxide $Cl_2O_7$** is obtained by the action of phosphorus pentoxide on perchloric acid,

$$2HClO_4 + P_2O_5 = Cl_2O_7 + 2HPO_3,$$

or by the action of chlorsulphonic acid on potassium perchlorate.

Chlorine heptoxide is a colourless oily liquid, unstable and explosive. It may be purified by distillation *in vacuo*. It is an acidic oxide, combining with water to form perchloric acid,

$$H_2O + Cl_2O_7 = 2HClO_4.$$

**1062a. Chlorine Tetroxide $(ClO_4)_x$.**—The action of iodine on silver perchlorate in ethereal solution yields a certain proportion of this oxide which has not yet been isolated pure. Its formula is probably but not certainly $Cl_2O_8$.

$$I_2 + 2AgClO_4 = 2AgI + Cl_2O_8.$$

**1063. Oxyacids of Chlorine.**—These include :—

| | |
|---|---|
| Hypochlorous acid . . . . | $HOCl$ |
| Chlorous acid . . . . . | $HClO_2$ |
| Chloric acid . . . . . | $HClO_3$ |
| Perchloric acid . . . . . | $HClO_4$ |

**1064. Hypochlorous Acid.**—Some hypochlorous acid is formed when chlorine reacts with water,

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl.$$

When chlorine reacts with a cold dilute solution of an alkali a mixture of chloride and hypochlorite results,

$$Cl_2 + 2KOH = KCl + KOCl + H_2O.$$

If the solution is hot chlorates (*q.v.*) result.

Hypochlorous acid itself is best prepared by the action of chlorine on a suspension of mercuric oxide. The water and chlorine give hypochlorous acid and hydrochloric acid. The former is too weak to attack mercuric oxide and remains in solution,

$$HgO + H_2O + 2Cl_2 \rightleftharpoons HgCl_2 + 2HOCl.$$

The resulting liquid is distilled and dilute hypochlorous acid passes over. This may be concentrated by evaporation in the cold, but solutions stronger than 5 per cent. decompose when distilled.

Hypochlorous acid forms a yellow solution. It has a peculiar chlorine-like smell. Both it and the hypochlorites (*q.v.*) have a remarkably strong germicidal action (§ 755).

Hypochlorous acid readily decomposes into hydrogen chloride and oxygen when heated or when exposed to light,

$$2HOCl = 2HCl + O_2.$$

Its solution is a strong oxidising agent.

The hypochlorites are of much more importance than the free acid. The chief of them are sodium hypochlorite NaOCl, and calcium chloro-hypochlorite, bleaching powder, $CaOCl_2$.

**1065. Sodium Hypochlorite NaOCl** may be made by passing chlorine into a cold dilute solution of sodium hydroxide or carbonate,

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O.$$

The solution cannot be concentrated, as it decomposes to form chlorate and chloride.

A weak solution is now made for the purpose of disinfection and bleaching by electrolysing common salt solution in such a way that the products, sodium hydroxide and chlorine, mix and react according to the equation given above.

Various kinds of cells are employed, but that shown in Fig. 178a is typical. Strong brine passes zig-zag fashion between conductive graphite plates ($a_1$, $b_1$, $a_2$, $b_2$, $a_3$, $b_3$, etc.) set in sockets formed in a

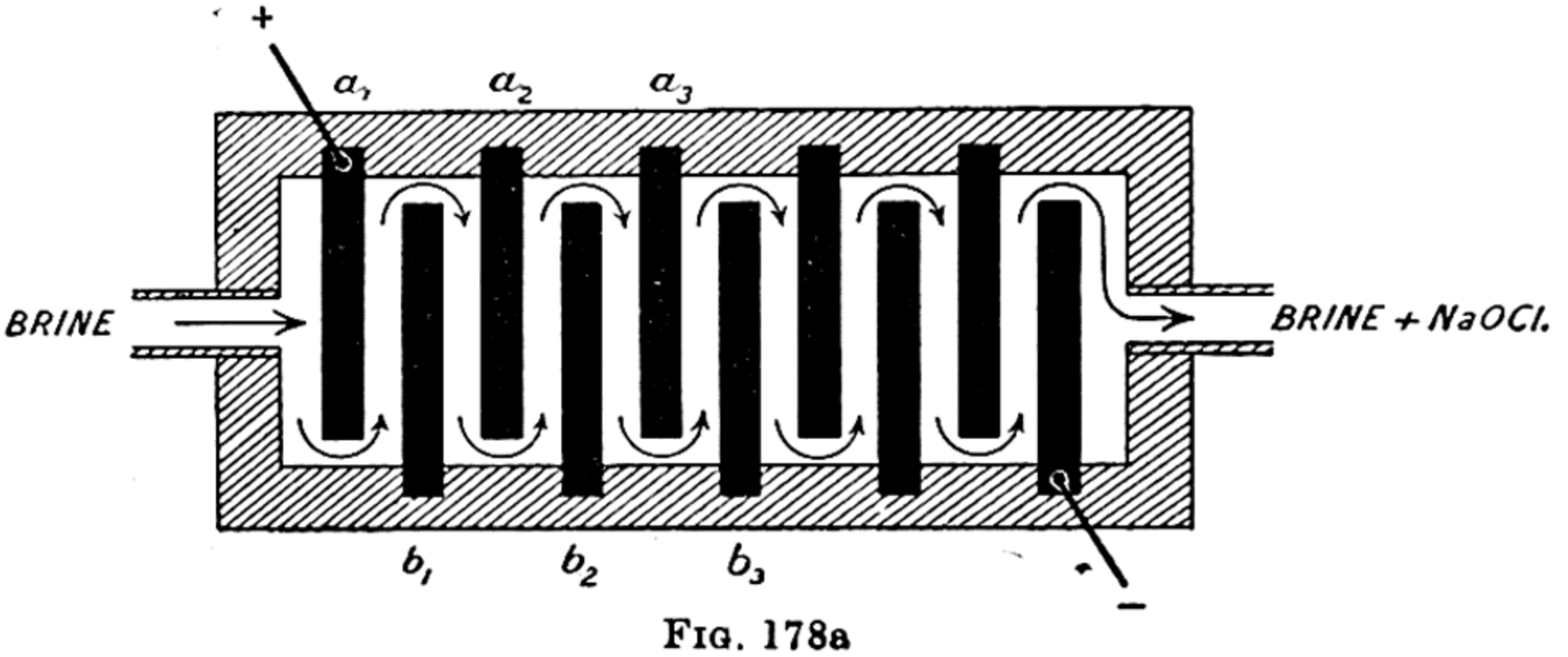



FIG. 178a

non-conducting trough. The end plates only are connected to the source of electricity. Each pair of plates forms in effect a separate electrolytic cell. Chlorine is liberated on the right-hand face of each plate and sodium hydroxide on the left-hand face ; these mix forming sodium hypochlorite. Solutions of greater strength than 1–2 per cent. NaOCl cannot be made in this way without loss of efficiency.

Sodium hypochlorite is much used for the bleaching of high quality vegetable fabrics, and of the wood pulp used as the raw material of the artificial silk trade.

Sodium hypochlorite solution is decomposed when heated, sodium chlorate and chloride being formed,

$$3NaOCl = NaClO_3 + 2NaCl.$$

The hypochlorites are all powerful oxidising agents. Thus with hydrochloric acid they give chlorine,

$$NaOCl + 2HCl = NaCl + H_2O + Cl_2.$$

They oxidise lead salts to lead peroxide (*q.v.*), arsenites to arsenates, etc. Hypochlorites liberate iodine from iodides and this reaction is used for their determination,

$$NaOCl + 2KI + 2HCl = NaCl + 2KCl + H_2O + I_2.$$

The value of sodium hypochlorite as a disinfectant is probably due to its action on the traces of ammonia present in contaminated water, etc. With this it forms chloramine $NH_2Cl$ (§ 755), which has a very powerful germicidal action.

**1066. Bleaching Powder, Chloride of Lime.**—Bleaching powder is made by the action of chlorine upon slaked lime, a reaction usually represented as,

$$Ca(OH)_2 + Cl_2 = CaOCl_2 + H_2O.$$

Chlorine, made by the electrolytic process, is led into the bottom of a circular concrete tower the interior of which is divided into numerous compartments by horizontal floors or ‘ beds.’ The lime enters at the top and is forced by rotating rakes to travel from floor to floor until it emerges at the bottom, having by this time been converted into bleaching powder. The temperature is carefully regulated by circulating warm water or chilled brine.

*The formula* of bleaching powder has been somewhat in dispute. It is in all probability a mixture and not a definite chemical compound. As made commercially it approximates in composition to $CaOCl_2$, but always contains some free lime. The formula $CaOCl_2$ was at one time supposed to represent $Ca(OCl)_2 + CaCl_2$, a mixture of calcium hypochlorite and chloride, but this is unlikely in view of

the fact that the material is not deliquescent, as is calcium chloride.

Bleaching powder is now thought to be a mixture of calcium hypochlorite $Ca(OCl)_2$ and *basic* calcium chloride $CaCl_2 . Ca(OH)_2 . H_2O$, which substance is not deliquescent.

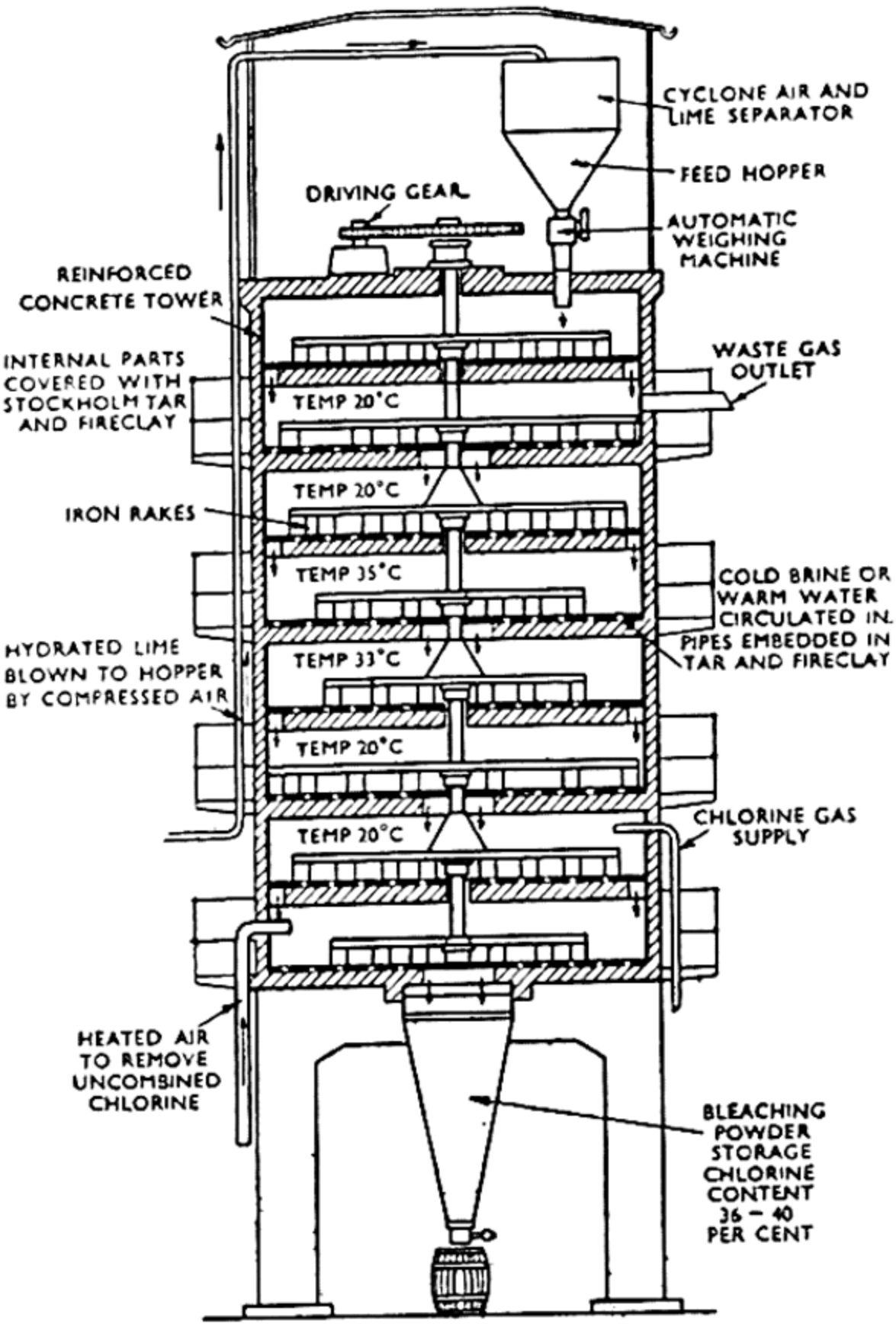



FIG. 178b.—Bleaching powder plant.

The formula $CaOCl_2$ may, however, still be used to express its chemical behaviour.

*Bleaching powder* is a white solid with a peculiar chlorine-like odour. It is soluble in cold water, but always leaves behind a residue of lime. A solution of bleaching powder, when boiled, forms calcium chlorate and chloride,

$$6CaOCl_2 = Ca(ClO_3)_2 + 5CaCl_2,$$

and so its solution should always be made up with cold water.

When acidified with any acid, chlorine is produced,

$$CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

Thus bleaching powder exposed to air evolves chlorine as a result of the action of carbon dioxide.

Its solution possesses the oxidising properties mentioned above under the heading of sodium hypochlorite. Its chief practical applications are as a bleaching agent and as a disinfectant.

**1066a. Methods of Bleaching.**—Cotton, which consists of the highly unreactive compound, cellulose, can safely be bleached by hypochlorites.

Wool and silk, on the other hand, consist of proteins, the amino-groups of which are readily attacked by hypochlorites; consequently their fibres would be weakened by these reagents.

Wool and silk are usually bleached by means of sulphurous acid, but sodium hydrosulphite is also sometimes employed. Both of these compounds bleach by reducing the colouring matter. Wool and silk can also be bleached by oxidation. Sodium peroxide, which when added to cold water yields sodium hydroxide and hydrogen peroxide, is used for this purpose and is especially useful for wool which is to be dyed in light shades.

Cotton is almost always bleached by hypochlorites. The hypochlorite employed may be

(1) a solution of bleaching powder,
(2) a solution of sodium hypochlorite made electrolytically (§ 1065),
(3) a solution of sodium hypochlorite made by passing chlorine from a cylinder into a weak solution of sodium carbonate.

The cotton fibre is coated with a natural resinous or waxy layer which is first of all removed by a prolonged boiling with alkalies—lime, soda-ash or caustic soda. This is performed in closed vessels called *kiers* in which a pressure of about one atmosphere is maintained.

The scoured material is then soaked for about six hours with the hypochlorite solution, at which stage most of the bleaching takes place. It is then treated with dilute sulphuric or hydrochloric acid. This removes particles of lime and also decomposes any hypochlorites left on the fabric, liberating chlorine, which completes the bleaching process. A thorough washing with water to remove calcium compounds, and with weak soap solution to remove traces of acid, completes the process.

**1067. Chlorous Acid and the Chlorites.**—Chlorous acid, $HClO_2$, is rarely met with. It is probably present in solutions of chlorine dioxide in water (§ 1061), but has not been isolated in the pure condition.

Sodium chlorite is made commercially by the action of chlorine dioxide, obtained from the action of acid upon chlorates, on caustic soda, lime and carbon.

$$4NaOH + Ca(OH)_2 + C + 4ClO_2 \rightarrow 4NaClO_2 + CaCO_3 + 3H_2O$$

Sodium chlorite is a powerful but stable oxidising agent, and is much used

in bleaching cellulose materials. The chlorites of some of the heavy metals have been prepared by precipitation.

**1068. Preparation of the Chlorates.**—The chlorates are prepared by the action of chlorine upon hot strong solutions of alkali. Potassium chlorate may be prepared in the laboratory by dissolving 15 gms. caustic potash in 50 c.c. water and saturating the hot solution with chlorine. Potassium chlorate, which is sparingly soluble in cold water, crystallises out on cooling, while the much more soluble chloride remains in solution,

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

On the large scale a strong solution of potassium chloride is electrolysed by passing it between a series of platinum-foil electrodes

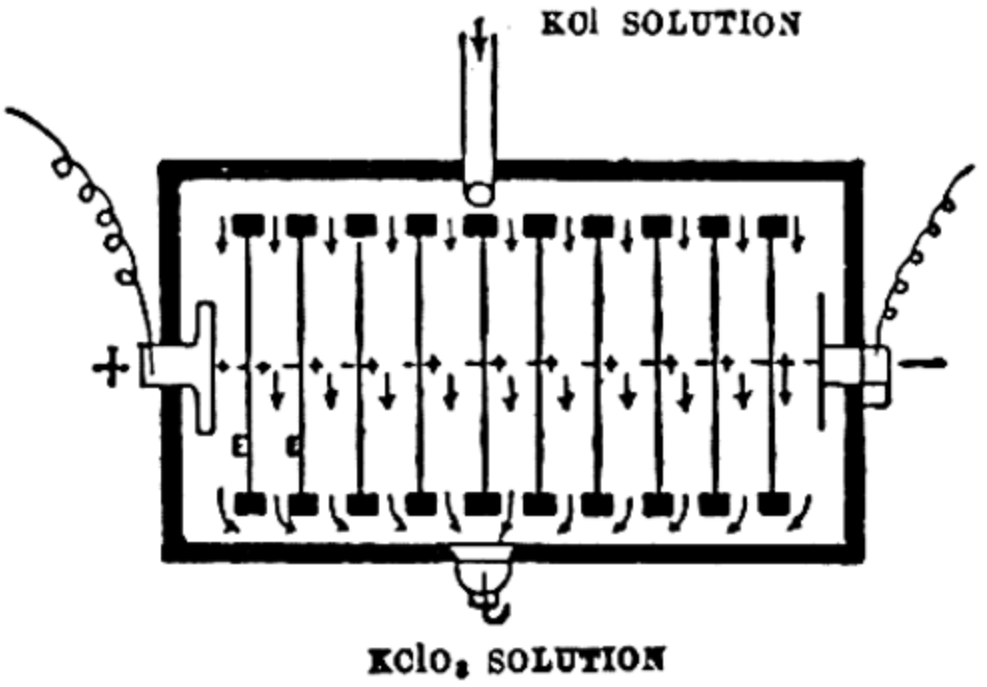



FIG. 179.—Electrolytic cell for preparation of potassium chlorate.

(Fig. 179, E, E), near enough together for the products of electrolysis, chlorine and caustic potash to react, giving the chlorate,

$$2K + 2H_2O = 2KOH + H_2$$
$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

The chlorate crystallises out when the liquors which leave the cell are cooled, and is purified by recrystallisation from water.

**1069. Chloric Acid.**—If a chlorate is treated with concentrated sulphuric acid the very explosive chlorine peroxide is formed. Accordingly, chloric acid is made from barium chlorate. This is prepared by passing chlorine into hot barium hydroxide solution,

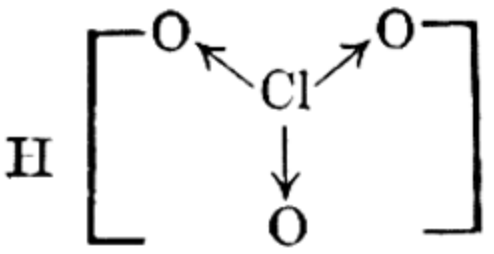
$$6Ba(OH)_2 + 6Cl_2 = Ba(ClO_3)_2 + 5BaCl_2 + 6H_2O.$$

The barium chlorate so formed is separated by crystallisation, and treated with an equivalent quantity of dilute sulphuric acid,

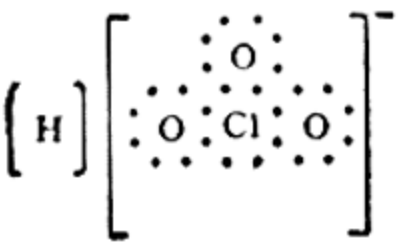
$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 \downarrow + 2HClO_3.$$

The barium sulphate is filtered off and the solution of chloric acid evaporated *in vacuo* until it contains about 40 per cent. of the acid, when it begins to decompose.

Chloric acid is probably $H - O - Cl\begin{matrix}\nearrow O \\ \searrow O\end{matrix}$ containing pentavalent chlorine or perhaps



*i.e.*,



*Properties.*—Chloric acid forms a colourless solution which, when heated, decomposes into perchloric acid, chlorine peroxide and water,

$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O.$$

It is a very powerful oxidising agent. Inflammable substances, such as wood or paper, burst into flame when the acid is dropped upon them, the acid itself decomposing explosively at the same time.

The dangerous character of chloric acid and its instability forbid the use of the pure substance as a laboratory reagent, but recently its solution has been used as a means of oxidising iodine to iodic acid (§ 1102).

**1070. The Chlorates.**—Potassium chlorate is the most important of these, and is made as described above. Sodium chlorate finds considerable use for making aniline-black, also as a weed killer.

**1071. Potassium Chlorate $KClO_3$** is a white crystalline salt, with a pleasant cooling taste. It is much used for throat lozenges, but these should not be over-indulged in, as in quantity the salt is poisonous. The practice of carrying loose matches and chlorate lozenges in the same pocket occasionally leads to alarming fires and serious burns. Potassium chlorate is sparingly soluble in cold water, of which 100 c.c. dissolve only 6 gms. at 15° C., but is freely soluble in hot water (100 gms. water dissolve 56·5 gms.).

The chlorates decompose when heated, giving off oxygen. This method of preparing oxygen and the catalytic effect of manganese dioxide upon it is discussed in § 861. The final result of the reaction is expressed by the equation

$$2KClO_3 = 2KCl + 3O_2.$$

The reaction (except in the presence of manganese dioxide) takes place in two stages. The chlorate first melts and then decomposes into the perchlorate and chloride,

$$4KClO_3 = 3KClO_4 + KCl.$$

The perchlorate having a higher melting point solidifies, but on further and stronger heating melts and itself decomposes,

$$3KClO_4 = 3KCl + 6O_2.$$

The chlorates are very vigorous oxidising agents. A mixture of a chlorate with almost any combustible material will burn explosively if ignited.

A mixture of phosphorus and potassium chlorate explodes with

most dangerous violence, gentle friction being sufficient to bring about explosion. A mixture of sulphur and potassium chlorate also explodes when struck with a hammer or ignited.

Treated with concentrated sulphuric acid the chlorates evolve the dangerously explosive chlorine peroxide. The heat of the reaction is usually enough to explode the gas, which decomposes with loud cracklings. This affords a test for a chlorate. The reaction should only be tried with the smallest amounts of material (*v.* under Chlorine Peroxide, § 1061).

Hydrochloric acid is oxidised by chlorates to chlorine, chlorine peroxide being also evolved in varying quantities,

$$2KClO_3 + 4HCl = 2KCl + Cl_2 + 2ClO_2 + 2H_2O.$$

Sir Humphry Davy named the gas ' euchlorine,' but he apparently recognised that it was not a pure compound. The mixture of hydrochloric acid and potassium chlorate is a useful reagent for destroying organic matter—as for example when the contents of a stomach are being tested for a metallic poison.

A solution of potassium chlorate in hydrochloric acid—much diluted—is used as a gargle for sore throats. Its efficiency is due to the antiseptic properties of the chlorine it contains.

The chlorates are distinguished from other oxidising agents by their oxidation of indigo to isatin. If an acidified solution of potassium chlorate is allowed to act on indigo the dye is bleached. This property is made use of in calico printing.

Numerous explosives contain potassium chlorate. Most mixtures of chlorates and combustibles are dangerously sensitive to shock, but the ' cheddites,' which are mixtures of potassium chlorate, nitrohydrocarbons (*e.g.*, mononitronaphthalene) and castor oil, are quite safe.

**1072. Perchloric Acid $HClO_4$.**—Potassium perchlorate is readily prepared by carefully heating potassium chlorate to 350° C. for some time. The mass is then boiled with about ten times its weight of water and allowed to cool. Any unchanged potassium chlorate remains in solution while the very sparingly soluble potassium perchlorate crystallises out.

From this salt perchloric acid is prepared by the action of concentrated sulphuric acid. The salt is distilled with sulphuric acid under reduced pressure and a crystalline mass of the monohydrate, $HClO_4 \cdot H_2O$, collects in the receiver. This substance, when redistilled, yields the pure acid.

Perchloric acid is a colourless fuming liquid. It is one of the four strongest acids. When pure it is very unstable, though less so than chloric acid. It decomposes with explosion when heated or often

merely on standing for a few days. Treated with phosphorus pentoxide it yields chlorine heptoxide $Cl_2O_7$ (§ 1062). When dropped on wood or paper it ignites them, and when dropped on charcoal, etc., oxidises it with explosive violence. The acid resembles sulphuric acid in evolving much heat when mixed with water.

A 20 per cent. solution of perchloric acid is quite safe and is an article of commerce. Its chief use is as a reagent for potassium. Potassium perchlorate is very slightly soluble in water (1·7 gms. per 100 gms. water at 15° C.), as are also the perchlorates of ammonium, rubidium and cæsium. It is practically insoluble in 50 per cent. alcohol. We may therefore test for a potassium salt by adding to the solution an equal volume of 20 per cent. perchloric acid and some alcohol. A white crystalline precipitate indicates potassium. Since several other perchlorates are also sparingly soluble, the test only serves to distinguish potassium salts from sodium salts or to detect the former in presence of the latter.

Potassium perchlorate and ammonium perchlorate have found considerable use in the manufacture of explosives, for which purpose they are well adapted, being more stable than chlorates and having a greater oxygen content. They are manufactured by electrolysing sodium chloride solution. The chlorate is first formed (§ 1068) and then the perchlorate. The solution of sodium perchlorate is mixed with potassium chloride, when the very sparingly soluble potassium perchlorate crystallises out. Ammonium perchlorate is made in a similar way.

**1072a. Chlorine halides.**—See § 1105.

## BROMINE Br, 79·916

The element bromine and its compounds have a close resemblance to chlorine and its corresponding compounds. The chief differences are to be found in the inferior affinity of bromine for metals and hydrogen, and in the fact that the oxides of bromine are even more unstable.

**1073. Historical.**—Bromine was discovered by Balard in 1826, by the action of chlorine on the residues resulting from the crystallisation of salt from sea water. Bromine narrowly escaped discovery by Justus von Liebig some years before, who, examining it superficially, pronounced it to be a chloride of iodine. The name bromine is derived from the Greek *βρῶμος*, a stench.

**1074. Occurrence.**—Bromine is never found free. The chief sources of the element are :—

(1) The mother-liquors left when salts have been crystallised from natural brine or native salt deposits. These may contain 0·2 per cent. to 1·5 per cent. bromine.

(2) Sea water which contains only about 70 parts per million.

Most of the world's bromine is made from the mother-liquors mentioned above. These include :—(*a*) the mother-liquors from which salt has been crystallised in certain salt mines in Ohio and other parts of America: and (*b*) the mother-liquors resulting from the separation of potassium chloride from the carnallite ($MgCl_2.KCl.6H_2O$) found in the Stassfurt salt deposits; the carnallite always contains some *brom-carnallite*, $MgBr_2.KBr.6H_2O$, and the mother-liquors accordingly contain from 0·2 to 0·3 per cent. bromide: (*c*) the liquors remaining after the separation of potassium chloride (as carnallite) from the water of the Dead Sea : (*d*) the mother-liquors remaining after common salt has been separated from ordinary sea-water. Extraction is performed by allowing these liquors to flow down a tower up which a current of chlorine passes. These react, giving bromine,

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

The bromine is then distilled out of the liquid by a current of steam and passes to condensers.

Bromine is now recovered on the large scale in the U.S.A. from sea-water by a rather similar process. Sea-water is treated with about 0·01 per cent. of sulphuric acid and the necessary quantity of chlorine. The bromine liberated is ' blown out ' by a current of air, and absorbed in towers fed with a solution of sodium carbonate. Here it forms sodium bromate and bromide, which, when acidified, liberate free bromine,

$$2Br^- + Cl_2 = Br_2 + 2Cl^-$$
$$3Br_2 + 3Na_2CO_3 = 5NaBr + NaBrO_3 + 3CO_2$$
$$5NaBr + NaBrO_3 + 6HCl = 6NaCl + 3H_2O + 3Br_2.$$

Crude bromine contains a proportion of chlorine and traces of iodine. A simple method of purification is to mix it with potassium bromide solution and distil it,

$$2KBr + Cl_2 = 2KCl + Br_2.$$

Very careful heating of the bromine to just below its boiling point will remove the chlorine in thirty-six to forty hours, and this method is now generally used.

In the laboratory bromine often needs to be purified. The bromine may be washed by shaking with water and then dissolved in very concentrated calcium bromide solution (so removing chlorine). On diluting the solution bromine again separates out. It is separated, dried over anhydrous calcium bromide and then over quicklime and finally distilled in a current of carbon dioxide.

**1075. Formula and Atomic Weight.**—The approximate atomic weight of bromine is 80, as shown from the vapour densities of its numerous volatile compounds and its position in the Periodic table, deduced from its likeness to chlorine. Its exact atomic weight has been determined by finding the weight of silver bromide precipitated from a solution containing a known weight of silver as nitrate. The formula of bromine is $Br_2$, as shown by its vapour density.

**1076. Physical Properties.**—Bromine is a dark-red liquid with a smell resembling that of chlorine, but more irritating to the nose and throat. Dropped on the skin it causes severe burns. Bromine boils at 59° C. and freezes at — 7·3° C. Its specific gravity is very high, 3·19, 0°/4° C. The density of the vapour (79·9) is also very high, corresponding to the formula $Br_2$.

Bromine is soluble in water to the extent of about 3 per cent. at room temperature. This solution, *bromine water*, is a useful oxidising agent, and is used in preference to chlorine water, which does not keep. When bromine water is cooled a solid hydrate, $Br_2.10H_2O$, is formed. A hydrate $Br_2.4H_2O$ also exists. Bromine is soluble in most organic solvents, carbon disulphide, ether, etc.

**1077. Chemical Properties.**—Bromine is a highly reactive element, much resembling chlorine in its chemical behaviour. It reacts, however, less vigorously with hydrogen, the reaction only occurring when the mixture is heated. Platinum catalyses the reaction,

$$Br_2 + H_2 = 2HBr.$$

Bromine reacts with sulphur, phosphorus, arsenic, antimony, tin, and most of the metals in the same manner as chlorine (*v.* § 1047), forming bromides of corresponding formula.

Bromine is an excellent oxidising agent. It does not react with water, but in presence of water and an oxidisable substance hydrogen bromide is formed and the oxygen of the water performs the oxidation,

$$Br_2 + H_2O + X = XO + 2HBr.$$

It performs most of the oxidising reactions attributed to chlorine in § 1048; and since it is much more convenient to handle it is commonly used in place of the latter element. In analysis it is frequently used in conjunction with nitric acid for oxidising sulphur and its oxy-salts to sulphates.

Bromine reacts with alkalis in the same manner as chlorine, hypobromites (§ 1082) and bromates (§ 1083) being formed.

Bromine has the same bleaching powers as chlorine but in a less degree. It is not, however, used for this purpose.

Free bromine may be detected by the colour of the vapour it

evolves on warming. This may be confused with nitrogen peroxide or chromyl chloride. To make identification certain the gas may be passed into water and the solution so obtained well shaken with a globule of carbon disulphide. The bromine dissolves in this and colours it orange. Nitrogen peroxide forms a colourless solution of nitrous and nitric acids, while chromyl chloride gives hydrochloric acid and yellow chromic acid, which latter is not dissolved by carbon disulphide.

Free bromine is determined volumetrically by causing it to react with excess of potassium iodide and titrating the equivalent of iodine liberated with sodium thiosulphate,

$$Br_2 + 2KI = 2KBr + I_2.$$

*Uses.*—Large quantities of bromine are employed in the manufacture of the coal tar dyes and other complex organic products, especially ethylene bromide.

**1078. Hydrogen Bromide, Hydrobromic Acid, HBr.**—Hydrogen bromide bears a strong resemblance to hydrogen chloride, differing chiefly in that it is dissociated into its elements when heated and also more easily oxidised.

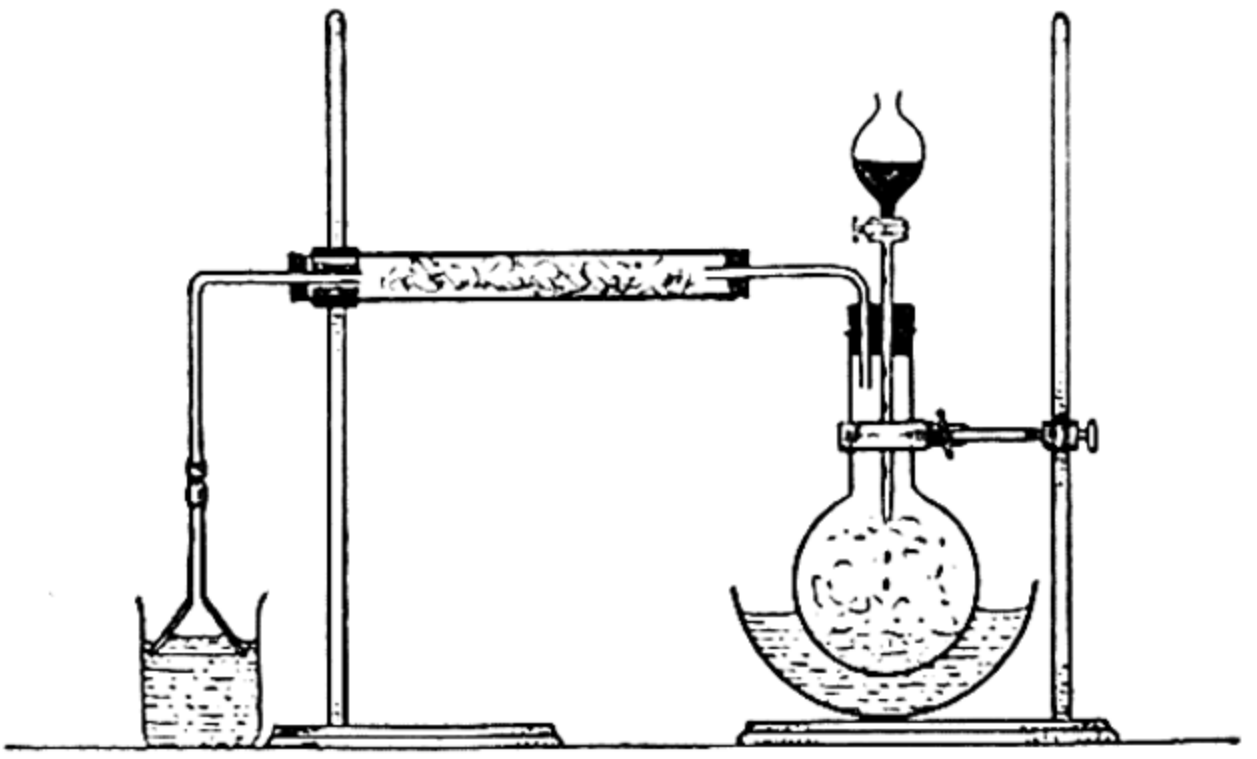


FIG. 180.—Preparation of hydrobromic acid.

*Preparation.*—(1) Hydrogen bromide cannot be satisfactorily prepared by the action of sulphuric acid on a bromide. Hydrogen bromide is formed by this reaction, but reacts in great part with the sulphuric acid, yielding free bromine,

$$H_2SO_4 + 2HBr = 2H_2O + SO_2 + Br_2.$$

Phosphoric acid may be employed instead of sulphuric acid, but is somewhat expensive,

$$H_3PO_4 + KBr = KH_2PO_4 + HBr.$$

(2) Hydrogen bromide is usually made by the action of phosphorus and bromine on water,

$$5Br + P + 4H_2O = H_3PO_4 + 5HBr.$$

The apparatus used is shown in Fig. 180. Bromine is placed in the dropping funnel and a mixture of red phosphorus (10 gms.) with twice its weight of water and some clean sand is placed in the flask. The bromine is allowed to drip into the phosphorus. Much heat is evolved and the flask should be cooled in water at first. The gas usually contains free bromine and this is best removed by passing it through a wide tube containing slightly damp red phosphorus smeared on bits of broken glass. The gas is collected over mercury or by displacement, but is more often required as a solution in water. The apparatus shown in Fig. 180 is suitable for dissolving it in water without fear of the water being sucked back.

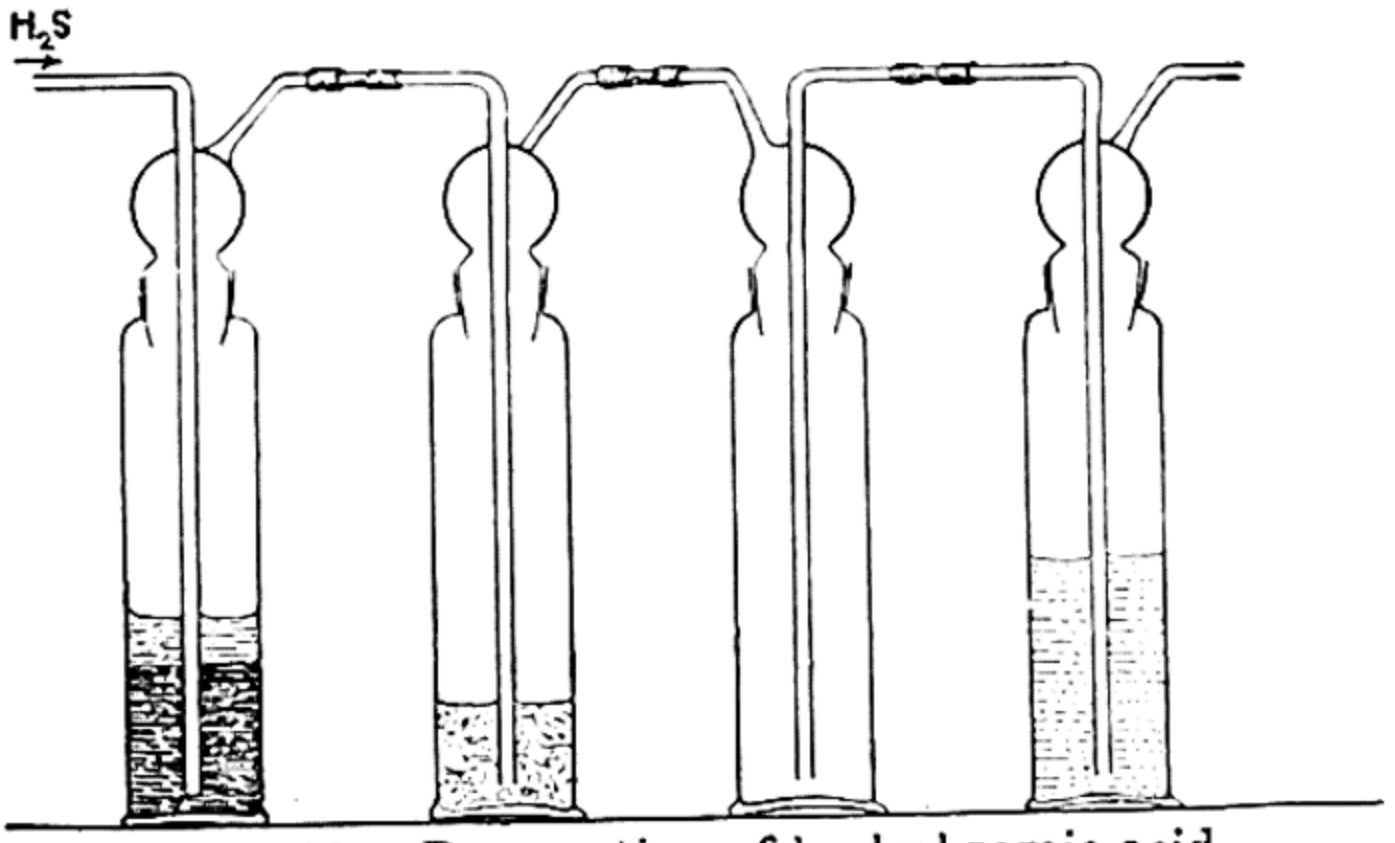



FIG. 181.—Preparation of hydrobromic acid.

The most convenient method of preparing the gas is, however, by the action of hydrogen sulphide on liquid bromine. A stream of the gas from a Kipp's apparatus is led into a wash bottle containing bromine covered with a thin layer of water (or better, hydrobromic acid). Hydrogen bromide and sulphur bromide are formed,

$$2H_2S + 3Br_2 = 4HBr + S_2Br_2.$$

The hydrogen bromide is led through a shallow layer of a suspension of red phosphorus in water (or better, hydrobromic acid) to remove bromine vapour. It may be absorbed in water as shown in Fig. 181, giving a solution of hydrobromic acid.

Hydrogen bromide is also conveniently made by bubbling hydrogen through a little warm bromine and conducting the gases over heated platinised asbestos. Any excess of the bromine may be removed by passing the gas over damp red phosphorus smeared on broken glass.

An excellent method is to run bromine slowly into benzene to which a little aluminium powder has been added. The gas is rapidly and freely evolved, but always contains some benzene vapour.

**1079. Formula.**—The arguments cited concerning the formula of hydrogen chloride (§ 48) apply with equal force to hydrogen bromide and show it to have the formula HBr.

**1080. Properties.**—Hydrogen bromide much resembles hydrogen chloride in physical properties. Thus it has a similar smell, fumes in air, and is extremely soluble in water. The saturated solution contains 69 per cent. of hydrogen bromide by weight. When heated its solutions behave like hydrochloric acid, forming a *constant boiling* mixture (§ 1055), which boils at 126° C. and contains about 48 per cent. of hydrobromic acid.

In its chemical properties it much resembles hydrogen chloride. The solution reacts in the same way with metals and their oxides, etc.

Hydrobromic acid is, however, a more easily oxidisable substance than hydrochloric acid. In addition to the reactions with the oxidising agents detailed in § 1056, as reacting with hydrochloric acid, it is also oxidised by sulphuric acid as described in § 1078 above. It is oxidised also by warm hydrogen peroxide, which does not affect hydrochloric acid. Hydrobromic acid finds a certain use in organic chemistry and is also occasionally used in medicine.

**1081. The Bromides**—The bromides resemble the chlorides in almost all particulars. They crystallise in the same forms. They are on the whole more soluble in water—silver bromide is an exception—and have higher melting points and boiling points.

Their chemical behaviour is similar but they are more readily oxidised than the corresponding chlorides. Thus with concentrated sulphuric acid they yield free bromine as well as hydrogen bromide. Potassium bromide was formerly used in medicine as a sedative, *i.e.*, a substance with a calming effect on disordered nerves, but since the potassium it contains had a depressant effect on the heart, sodium bromide is now used. Several good tests for bromides are available. If the salt is mixed with manganese dioxide and sulphuric acid, bromine is evolved if a bromide is present. The vapour may be passed into water and identified as in § 1077. If the salt is soluble a few drops of chlorine water (or acidified bleaching powder solution) may be added and the solution shaken with carbon disulphide. An orange coloration in the latter indicates bromine,

$$2KBr + Cl_2 = 2KCl + Br_2.$$

**1082. Hypobromites.**—When bromine is added to cold caustic soda solution sodium hypobromite results,

$$2NaOH + Br_2 = NaBr + NaOBr + H_2O.$$

The properties of the hypobromites are similar to those of the hypochlorites. They are very easily converted into bromates when heated,

$$3NaOBr = 2NaBr + NaBrO_3.$$

An alkaline solution of sodium hypobromite is used in the determination of urea in urine. It reacts with urea, forming carbon dioxide, which combines with the free alkali, and nitrogen, which is collected and measured,

$$CO(NH_2)_2 + 3NaOBr = CO_2 + N_2 + 2H_2O + 3NaBr.$$

**1083. The Bromates.**—The bromates resemble the chlorates in almost all particulars. They are prepared in the same way and have similar oxidising qualities.

A mixture of bromate and bromide is sometimes used instead of a standard volumetric solution of bromine, which, owing to the volatility of the latter, is unreliable. A solution of $\frac{1}{6}$ gm.-mol. of potassium bromate with an excess ($> \frac{5}{6}$ gm.-mol.) of potassium bromide yields, when acidified with HCl, a normal solution of bromine,

$$KBrO_3 + 5KBr + 6HCl = 3Br_2 + 3H_2O + 6KCl.$$

*Bromic acid* has been made by methods analogous to those used for the preparation of chloric acid, which it much resembles. Neither perbromates nor perbromic acid are known.

**1084. Oxides of Bromine.** *Bromine Monoxide.*—The action of bromine on specially reactive mercuric oxide (formed by precipitating mercuric chloride with very dilute sodium hydroxide at 50° C.) produces a certain proportion of bromine monoxide,

$$HgO + 2Br_2 = HgBr_2 + Br_2O.$$

It can be freed from bromine by absorbing the latter with pure alkali hydroxide. It is a dark brown unstable gas which breaks up rapidly even at 0° C.

*Bromine dioxide* $BrO_2$ has been made by passing a mixture of bromine with excess of oxygen through an ozoniser at liquid-air temperature. It is a yellow solid which decomposes about 0° C., forming bromine monoxide and a higher oxide, probably *bromine heptoxide* $Br_2O_7$.

An oxide of the formula $(Br_3O_8)_n$ has been formed by the action of ozone on bromine vapour at temperatures below 0° C. It is very unstable.

**1085. Bromine Halides.**—See § 1105.

## IODINE I, 126·92

Iodine and its compounds have the general characteristics of the halogens. The reactivity of the element with hydrogen and the metals is decidedly less, and the stability of its oxygen compounds more pronounced than is the case with bromine. A few indications of metalloid characteristics appear in iodine.

**1086. History.**—Iodine was first prepared in 1812 by the action of sulphuric acid on the mother liquors, resulting from the crystallisation of *kelp*, the ash obtained by burning seaweed. The name iodine, ἰοειδής, violet coloured, was given it on account of the violet colour of its vapour.

**1087. Occurrence.**—Iodine is never found free in Nature. Minute traces of its compounds are found in all living creatures, in many minerals, and notably in sea water.

There are two chief sources of iodine :—

(1) Certain seaweeds extract iodine from sea water, and the ash of these when burned contains about 0·5 per cent. of iodine as potassium and sodium iodides.

(2) The nitrate deposits of Chili (*v.* p. 274) contain some 0·2 per cent. of sodium iodate, which is worked up for iodine.

(1) *Iodine from Kelp.* Seaweeds vary greatly in their iodine content. Those uncovered by the tide yield little iodine, but the 'red

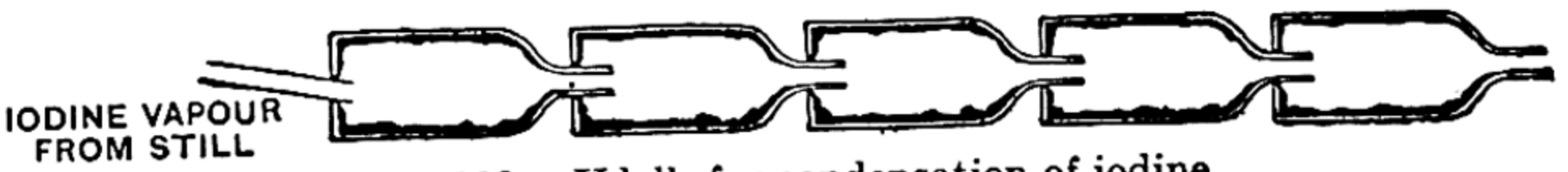



Fig. 182.—Udells for condensation of iodine.

wracks,' dark-red ribbon-like seaweeds, often driven ashore after storms, contain a remunerative quantity. The seaweed is roughly dried and burned, and a fused mass of salts, consisting chiefly of potassium sulphide and chloride, sodium carbonate and some 1 to 1·5 per cent. of the iodides of these metals, remains. This 'kelp' is then extracted with water and the solution is crystallised, when potassium sulphate, potassium chloride, and sodium chloride crystallise. The mother-liquor contains the iodides together with bromides, sulphides, etc. It is first treated with sulphuric acid to get rid of the latter and then distilled with manganese dioxide and sulphuric acid. The iodine vapours are condensed in *udells* (Fig. 182), stoneware bottles, of which the neck of one enters a hole in the base of the next. The iodine is purified by sublimation as described below.

(2) Much more important is the extraction of iodine from the mother-liquors from which sodium nitrate has been crystallised in the course of its manufacture from the Peruvian and Chilean mineral *caliche.*

The mother-liquor contains sodium iodate $NaIO_3$, together with sodium nitrate, sulphate, chloride, and some magnesium salts. To this liquid is added the precise quantity of sodium bisulphite needed to precipitate the iodine. The reactions are probably (*a*) the formation of iodide, and (*b*) the reaction of this with the iodate,

(*a*) $$NaIO_3 + 3NaHSO_3 = NaI + 3NaHSO_4.$$

(*b*) $$NaIO_3 + 5NaI + 6NaHSO_4 = 3H_2O + 6Na_2SO_4 + 3I_2.$$

The solution is neutralised and the iodine, which is nearly insoluble, settles to the bottom. It is washed with water, pressed roughly dry and then sublimed into udells, much as in the kelp process.

Iodine is further purified by mixing it with a little potassium iodide (to remove chlorine) and subliming it.

**1088. Recovery of Iodine Residues in the Laboratory.**—Iodine is costly enough to be worth recovering. Many laboratories do not throw away liquids containing iodine but keep them in a stock bottle. After three or four litres have accumulated, a strong solution of potassium dichromate in dilute sulphuric acid (1 : 3) may be added, cooling if necessary. The precipitated iodine is filtered off, washed, dried in a desiccator and sublimed,

$$K_2Cr_2O_7 + 11H_2SO_4 + 6KI = 8KHSO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

The sublimation of iodine is best performed in the laboratory by placing it in a shallow crystallising dish, which is well bedded in a large sand bath. The dish is covered with a glass plate, the joints being made nearly air-tight

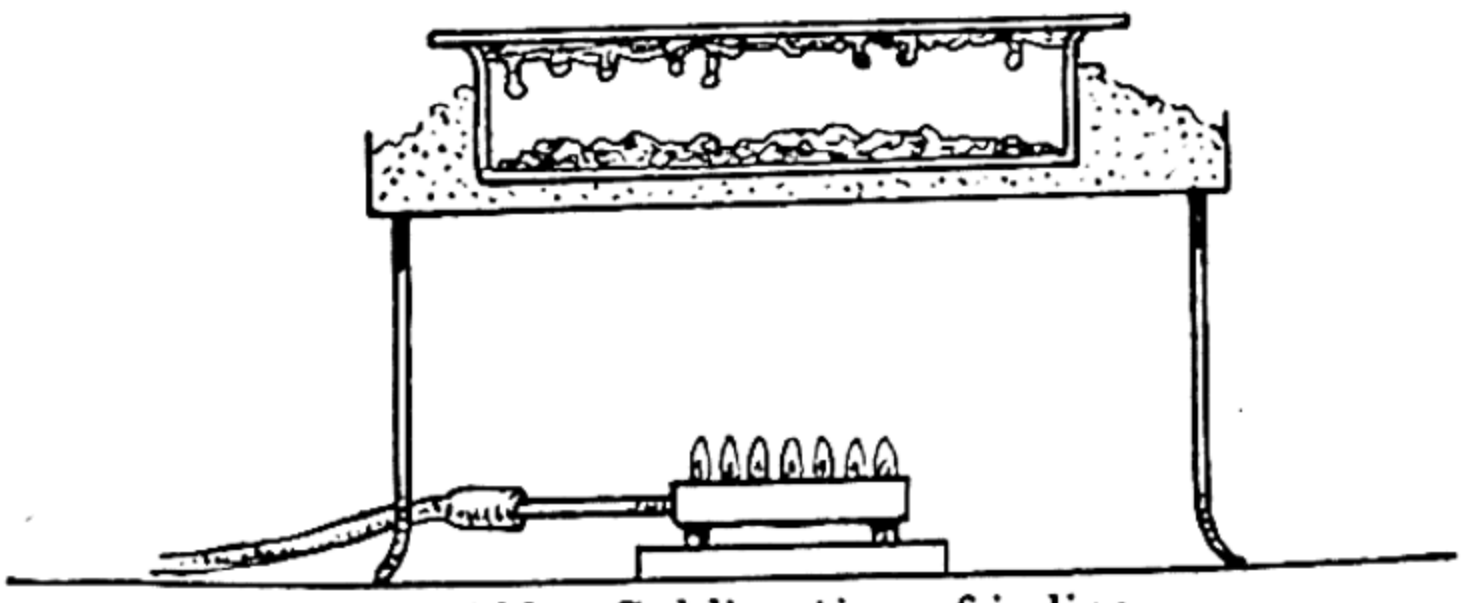


Fig. 183.—Sublimation of iodine.

with strips of gummed paper. The dish is gently heated so that the iodine slowly sublimes into the lid during several days. The plate may be cooled by means of damp blotting paper.

A better method of purification is to place the iodine in a covered beaker and add a little concentrated potassium iodide solution. The mixture is heated till the iodine melts and is then allowed to cool. This process removes any chlorine. The iodine may then be washed and roughly dried on a Buchner funnel. The iodine is finally dried in a desiccator.

**1089. Physical Properties.**—Iodine is a grey-black solid of metallic lustre. It crystallises in rhomboidal plates. The smell of iodine resembles that of chlorine. In large quantities the vapour is intensely irritating to the eyes and nose. Iodine melts at 114° C. and boils at 184° C. It vaporises rapidly, even below its melting point, giving off a vapour of a fine deep violet tint. The vapour has a density of 128 ($H_2 = 1$) and is therefore nearly nine times as heavy as air.

Iodine is sparingly soluble in water, the saturated solution containing about 0·015 per cent. of the element. It is, however, readily

dissolved by a solution of potassium iodide, with which it forms a loose compound, $KI_3$. This compound is so readily decomposed that the solution behaves like a solution of free iodine. Iodine is readily soluble in carbon disulphide, chloroform, and various hydrocarbons, forming violet solutions; in alcohol, ether and oxygen-containing solvents in general it dissolves to form a brown solution. It appears that the iodine in the brown solutions is loosely combined with the solvent and in one or two cases the compound has been isolated.

**1090. Chemical Properties.**—Iodine does not react with oxygen. With hydrogen it reacts, forming an equilibrium mixture of hydrogen iodide, hydrogen and iodine,

$$H_2 + I_2 \rightleftharpoons 2HI,$$

the reaction being far from complete and very slow. It may be hastened by the presence of platinum, which is an excellent catalyst.

Iodine reacts less readily with the other elements than do the remainder of the halogens. Thus, among the non-metals, it reacts directly only with phosphorus, chlorine and fluorine. The metals react with it vigorously, but much less vigorously than with chlorine or bromine, which displace iodine from its compounds with elements other than oxygen.

The oxidising action of iodine is much feebler than that of the other halogens. None the less it oxidises sulphites to sulphates, arsenites to arsenates, hydrogen sulphide to sulphur, hydrogen iodide being formed in each case,

$$I_2 + H_2S = 2HI + S$$
$$Na_3AsO_3 + I_2 + H_2O = Na_3AsO_4 + 2HI.$$

These reactions are utilised in volumetric analysis for the determination of arsenic, sulphites and hydrogen sulphide by titrating them with standard iodine solution.

The reaction of iodine with starch is of interest. In presence of even one part per million of iodine starch solution is coloured blue. The nature of the compound formed is unknown. The starch solution should be fresh, as starch is easily hydrolysed to form compounds which do not give this colour.

The reaction of iodine with sodium thiosulphate to form sodium tetrathionate has found much use in analysis,

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

It is an ideal reaction for volumetric analysis. It is instantaneous, requires no heat, and the fading colour of the iodine marks the progress of the titration. The end-point is marked by adding a few

drops of starch solution to the iodine and continuing the addition of thiosulphate until the blue colour vanishes.

Sodium thiosulphate is readily obtained in a state of high purity, and can be made with great ease into an accurate standard solution.

The method is not only valuable for determining iodine but also for determining any oxidising agent. Chlorine, bromine, cupric salts, hypochlorites, etc., all react with iodides (*q.v.*), giving iodine and water. To determine the proportion of any of these substances in a solution, a known volume of it is run into excess of potassium iodide solution, liberating iodine. The solution is then titrated with sodium thiosulphate, and from the quantity of this used the weight of iodine produced, and consequently the weight of oxidising agent used may be calculated.

**1091. Tests for Iodine.**—The starch test has been mentioned above. If a solution containing iodine be shaken with a drop of carbon disulphide the iodine will dissolve in the drop and give it a violet colour.

**1092. Uses of Iodine.**—Iodine is used in the manufacture of certain coal-tar dyes. It finds considerable use in medicine. It is an excellent disinfectant and is used as 'tincture of iodine'—a 10 per cent. solution of iodine in dilute alcohol—for the treatment of small wounds. Iodine in the form of iodides has a beneficial but obscure effect on many diseases. The thyroid gland, which lies on either side and in front of the windpipe, secretes a peculiar substance, thyroxin, which contains iodine and helps to regulate the rate at which the bodily processes take place. A deficiency of this substance during infancy causes idiocy—cretinism—and a train of peculiar symptoms. Both cretinism and goitre, a swelling of the thyroid gland, can be caused by the drinking of water in which iodine is deficient.

**1093. Atomic Weight of Iodine.**—The atomic weight of iodine is nearly 127, as shown by the fact that not less than 127 gms. of iodine are contained in the gram-molecule of any of the many volatile or soluble iodine compounds of which the molecular weight can be determined. Its character as a halogen, moreover, necessitates a place in the Periodic table corresponding to an atomic weight of about 127 or about 218, and only the former value is a possible multiple of its equivalent, 127.

The atomic weight may be determined by means of the ratio, Ag : AgI (cf. § 70), or by the decomposition of iodine pentoxide, the oxygen being absorbed by red-hot copper and the iodine condensed. The latter method is direct, while the former depends on the accurately known value for silver. The best value appears to be 126·92.

**1094. Hydrogen Iodide, Hydriodic Acid, HI.**—Hydrogen iodide cannot be made by the action of acids upon iodides. Its solution is usually prepared by the action of hydrogen sulphide upon iodine,

$$H_2S + I_2 = 2HI + S.$$

The iodine is suspended in water and the gas passed through the mixture. When the iodine has disappeared the sulphur is filtered off and the liquid is distilled.

The gas is best made by the action of water on phosphorus iodide. Red phosphorus and iodine are mixed in a dry flask, and water is

$$PI_3 + 3H_2O = H_3PO_3 + 3HI$$

slowly added from a tap-funnel. The gas is freed from iodine by the action of damp red phosphorus and dried by means of anhydrous calcium iodide.

The gas is also made by passing hydrogen over heated iodine. The mixture of hydrogen and iodine vapour is passed over heated[1] platinised asbestos, which acts as a catalyst. Any excess of iodine is removed by condensation and by passing the gas over some

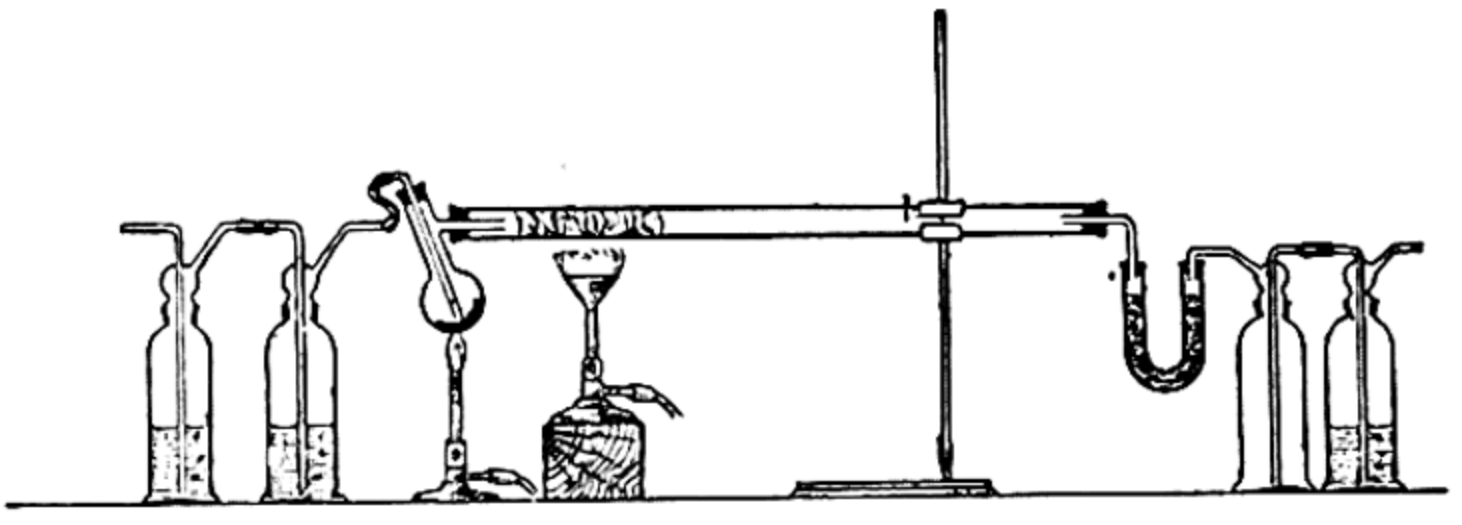


FIG. 184.—Preparation of hydriodic acid.

damp red phosphorus. The resultant gas may be dissolved in water, the arrangement of two wash-bottles, as illustrated in Fig. 184, avoiding any possibility of the water being sucked back into the heated tube.

**1095. Properties.**—Hydrogen iodide is a colourless gas which fumes in air. It has an irritating odour. It is extremely soluble in water, the solution saturated at 10° C. containing 70 per cent. of the acid by weight. When distilled a constant boiling mixture (§ 1055) is formed, containing 57 per cent. of hydrogen iodide by weight.

Hydrogen iodide is readily decomposed when heated,

$$2HI \rightleftharpoons H_2 + I_2.$$

It has the usual properties of an acid (pp. 194 *seq.*), and is, in addition, a strong reducing agent. Almost every oxidising agent will

[1] Air must be displaced by hydrogen before heating is commenced.

oxidise it to iodine and water and on this fact is based the method of determining oxidising agents volumetrically (§ 1090).

The oxidising agents which affect hydrogen iodide include those which affect hydrogen bromide, *e.g.*, (*a*) oxygen, (*b*) hydrogen peroxide, (*c*) nitric acid, (*d*) persulphates, (*e*) chlorine, (*f*) sulphuric acid, and also the following, which do not affect the other hydrogen halides: (*g*) cold dilute nitrous acid, (*h*) ferric salts, (*i*) nitrates in dilute acid solution, (*j*) bromine, (*k*) cupric salts. Iodine is in every case liberated.

The equations are given below :—

(*a*) $O_2 + 4HI = 2H_2O + 2I_2$.

(*b*) $H_2O_2 + 2HI = 2H_2O + I_2$.

(*c*) $2HNO_3 + 6HI = 4H_2O + 2NO + 3I_2$ (other nitrogen oxides may result).

(*d*) $K_2S_2O_8 + 2HI = K_2SO_4 + H_2SO_4 + I_2$.

(*e*) $Cl_2 + 2HI = 2HCl + I_2$.

(*f*) $\left\{\begin{matrix} H_2SO_4 + 8HI = H_2S + 4H_2O + 4I_2 \\ H_2SO_4 + 6HI = 4H_2O + S + 3I_2 \end{matrix}\right\}$

(*g*) $2HNO_2 + 2HI = 2H_2O + 2NO + I_2$.

(*h*) $2FeCl_3 + 2HI \rightleftharpoons 2FeCl_2 + I_2 + 2HCl$.

(*i*) As (*c*) above.

(*j*) $Br_2 + 2HI = 2HBr + I_2$

(*k*) $2CuSO_4 + 4HI = 2H_2SO_4 + Cu_2I_2 + I_2$.

It is a useful reducing agent, particularly in organic chemistry.

**1096. The Iodides.**—The iodides in general resemble the chlorides and bromides except in respect of their ready oxidation to iodine. Many of them have characteristic colours, such as the iodides of lead, mercury, bismuth and silver.

They are recognised by their giving free iodine when warmed with concentrated sulphuric acid and manganese dioxide. The violet vapour of the iodine produced is very easily noticed. In solution iodides may be detected by adding an oxidising agent, such as chlorine or acidified hydrogen peroxide, and shaking with a little carbon disulphide. The iodine liberated colours the carbon disulphide violet. The starch test may also be applied to the solution after addition of an oxidising agent.

**1097. Potassium Iodide** is the most important iodine compound. It is made from iodine by mixing iron borings, iodine and water and so preparing iron iodide,

$$Fe + I_2 = FeI_2.$$

To the solution of iron iodide is added potassium carbonate,

$$FeI_2 + K_2CO_3 = FeCO_3 + 2KI.$$

The insoluble ferrous carbonate is filtered off and the iodide is evaporated until it crystallises. For medical purposes it should contain no iodate, which is decidedly poisonous. The addition of dilute acid to the solution detects the presence of iodate, for a mixture of iodate, iodide and acid liberates free iodine (§ 1102), readily detected by the starch test.

**1098. Mercuric Iodide $HgI_2$** is of interest as existing in two forms and as having a remarkable double salt with potassium iodide $K_2HgI_4$ (§ 456).

**1099. Cuprous Iodide $Cu_2I_2$.**—Iodides reduce cupric salts and consequently cupric iodide is not formed. On addition of an iodide to a cupric salt, white insoluble cuprous iodide is precipitated and iodine is set free,

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4.$$

The reaction is used for the volumetric determination of copper.

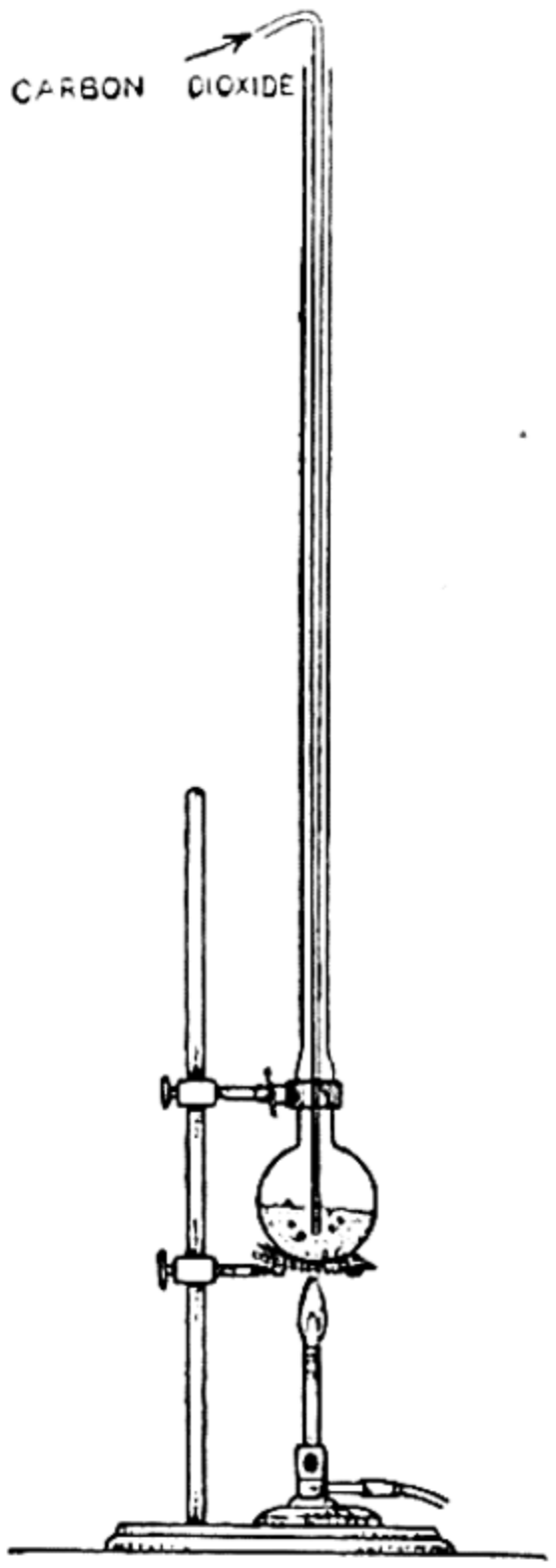



FIG. 185.—Preparation of iodic acid.

**1100. Oxides and Oxyacids of Iodine.**—The oxides, $I_2O_4$, $I_4O_9$ and $I_2O_5$ exist. Iodic acid $HIO_3$ is known in the free state, and periodic acids of formulæ $H_5IO_6$, $HIO_4$, and $H_4I_2O_9$ have been prepared.

**1101. Iodine Pentoxide** is the only important oxide of iodine. It is made by gently heating iodic acid $HIO_3$,

$$2HIO_3 = H_2O + I_2O_5.$$

It is a white solid and is much the most stable of the halogen oxides. With water it forms iodic acid,

$$H_2O + I_2O_5 = 2HIO_3.$$

**1102. Iodic Acid $HIO_3$** is prepared by the action of concentrated nitric acid or of chloric acid upon iodine,

$$10HNO_3 + I_2 = 2HIO_3 + 4H_2O + 10NO_2.$$

Concentrated colourless nitric acid (90 c.c.) and iodine (30 gms.) are placed in a round flask on to which has been sealed a long wide glass tube to act as a reflux condenser. A slow current of carbon dioxide is passed to carry off oxides of nitrogen, which may reduce the iodic acid. The mixture is boiled (bumping may be troublesome) until the iodine has disappeared. The acid crystallises out and is filtered off through asbestos and recrystallised from a little water.

The best method of preparing iodic acid and iodine pentoxide employs chloric acid $HClO_3$ as oxidising agent.

62·5 gms. of $Ba(ClO_3)_2 . H_2O$ are dissolved in 100 c.c. of nearly boiling

water and a trifle less than the theoretical quantity of hot diluted sulphuric acid (equal vols. conc. acid and water) is added. The solution of chloric acid is decanted or filtered off. Fifty grams of iodine are placed in a 500 c.c. flask, fitted with some arrangement for passing a slow current of air, and a 3 per cent. excess of the chloric acid solution is added. The flask is connected to some arrangement for absorbing chlorine and gently heated to start the reaction,

$$I_2 + 2HClO_3 = 2HIO_3 + Cl_2.$$

The reaction completes itself in some twenty minutes. The resulting solution is filtered and cautiously evaporated to dryness. The iodic acid is best converted into iodine pentoxide by heating to a temperature of 235°–240° C. in a tube through which a slow current of dry air is passed. The yield is almost theoretical.

It forms white crystals, which decompose when heated, forming iodine pentoxide as mentioned above.

It reacts with reducing agents, giving iodine. With sulphurous acid an interesting delayed reaction takes place.

With hydriodic acid, iodic acid forms iodine and water. A method of titrating acids has been based on this reaction. If potassium iodate and iodide solutions are mixed there is no reaction. If, however, an acid is added they react, liberating one atom of iodine for .

$$5KI + KIO_3 + 6HCl = 6KCl + 3I_2 + 3H_2O,$$

each atom of replaceable acid hydrogen added. The method is useful where there is an objection to adding an alkali during titration.

The 'time-reaction' between iodic acid and sulphurous acid is of interest. If solutions of these substances are mixed, no reaction appears to occur for some seconds or minutes, then suddenly the solution becomes coloured with iodine (conveniently demonstrated by adding a little starch). The phenomenon is due to the reduction of iodic acid to hydriodic acid and the reaction of these to form iodine. The iodine is, however, removed by the sulphurous acid as long as any of the latter remains. When the sulphurous acid has all been exhausted, free iodine appears,

$$HIO_3 + 3H_2SO_3 = HI + 3H_2SO_4$$
$$HIO_3 + 5HI = 3I_2 + 3H_2O$$
$$I_2 + H_2SO_3 + H_2O = 2HI + H_2SO_4.$$

It will be seen that rather less than two molecules of sulphurous acid to one of iodic acid is a suitable proportion.

**1103. The Iodates** resemble the chlorates in many ways. They are decomposed by heat but less readily than the bromates or chlorates.

**1104. Periodic Acids.**—Acids $HIO_4$, $H_5IO_6$, $H_4I_2O_9$ have been isolated as white solids. Iodine heptoxide remains unknown. The simplest, salts such as $KIO_4$, $AgIO_4$ correspond to the perchlorates, but others, such as $Ag_5IO_6$, $Na_2H_3IO_6$ are also known.

**1105. Interhalogen Compounds.**—Until recently it was thought that very few of these existed, but recently many have been discovered. These may be summarised in a table as below.

| | Name. | Formula. | Colour (of gas). | B.P.° C. |
|---|---|---|---|---|
| Type AB. | Chlorine monofluoride | ClF | Almost colourless. | —100 |
| | Bromine monofluoride | BrF | Pale red. | 20 |
| | Bromine monochloride | BrCl | Pale brown. | 5 |
| | Iodine monochloride . | ICl | 2 forms solid: red and brown. | 97·4 |
| | Iodine monobromide . | IBr | Dark red. | 116 |
| Type $AB_3$ | Chlorine trifluoride . | $ClF_3$ | Colourless. | 13 |
| | Bromine trifluoride . | $BrF_3$ | Colourless. | 127 |
| | Iodine trichloride . | $ICl_3$ | Lemon yellow solid vapour$\longrightarrow ICl + Cl_2$ | M.P. 101 (16 atm.) |
| Type $AB_5$ | Bromine pentafluoride | $BrF_5$ | Colourless. | 40·5 |
| | Iodine pentafluoride . | $IF_5$ | Colourless. | 97 |
| Type $AB_7$ | Iodine heptafluoride . | $IF_7$ | Colourless. | 4·5 |

These compounds are made by the direct action of the halogens on each other or on a lower halogen halide.

They are, as a rule, highly reactive and behave much as a mixture of the individual halogens.

**1105a. Salts of Iodine.**—Iodine, as the heaviest member of the halogen family, might be expected to show some metallic properties.

There are a number of compounds in which iodine is electro-positive. These include the iodine chlorides (*v.s.*); iodine phosphate $IPO_4$; basic iodous sulphate $(IO)_2SO_4 . \frac{1}{2}H_2O$; iodine trichloracetate $I(CCl_3 . COO)_3$; iodine nitrates $I(NO_3)_3$, $INO_3$. The oxide $I_2O_4$ is believed to be basic iodous iodate $IO . IO_3$. Iodine in alcoholic solution fairly certainly gives $I^-$ and $I^{+++}$ ions,

$$2I_2 \rightleftharpoons 3I^- + I^{+++}.$$

On addition of alcoholic silver nitrate we have

$$3Ag^+ + 3NO_3^- + 3I^- + 3I^{+++} = 3AgI\downarrow + I(NO_3)_3.$$

The iodine nitrate remains in solution.

## ASTATINE At, 210

This element is formed by the $\beta$-ray decay of polonium (Po, 218). Astatine is radioactive and has not been obtained in quantities sufficient for investigation.

## GENERAL COMPARISON OF THE PROPERTIES OF THE STABLE HALOGENS

| Property. | Fluorine. | Chlorine. | Bromine. | Iodine. |
|---|---|---|---|---|
| Atomic weight | 19·0 | 35·46 | 79·9 | 126·9 |
| State | Gas. | Gas. | Liquid. | Solid. |
| Colour of vapour | Pale-yellowish. | Yellowish-green. | Red-brown. | Violet. |
| Smell | Irritating. | Irritating and choking. | More irritating. | Still more irritating. |
| M.P. | −233° C. | −102° C. | −7·3° C. | 114° C. |
| B.P. | −187° C. | −33·5° C. | 59° C. | 184° C. |
| Density of solid or liquid | *c.* 1·0 | 1·33 | 3·19 | 4·93 |
| Solubility in 100 gms. water by weight at 15° C. | Decomposes water. | 0·82 gm. | 3·5 gms. | 0·015 gm. |
| Reaction— with hydrogen | Explosive even in dark. | Explosive in light. In darkness only if ignited. | Requires heat to cause combination. | Partial and slow even when heated. |
| with non-metals | All react except nitrogen and oxygen. | All react except nitrogen, oxygen and carbon. | All react except nitrogen, oxygen, silicon, carbon. | Only phosphorus, arsenic and halogens react. |
| with metals | Almost all metals burn. | Many metals burn. All attacked. | All metals attacked. A few burn. | All metals attacked except platinum. |
| with water | Instantly forms $H_2F_2$ and $O_2$. | Slowly forms HCl and $O_2$. | No reaction. | No reaction. |
| oxidising agents | Unaffected. | Unaffected. | Possibly forms an oxide with ozone. | Nitric acid oxidises it to the iodic acid. |
| reducing agents. | All react. | All react. | All react. | Most reduce it to hydrogen iodide. |
| Bleaching action | — | Good. | Moderate. | — |
| *Hydrides* | $(HF)x$ | HCl | HBr | HI |
| B.P. | 19·4° C. | −83° C. | −69° C. | 37° C. |
| Solubility in water | Miscible. | 46 per cent./0° C. | 69 per cent. | > 70 per cent. |
| Composition of constant boiling mixture. | 37 per cent. | 20·2 per cent. | 47·5 per cent. | 57 per cent. |
| Effect of heat | None. | Decomposed at about 1,500° C. | Decomposed at about 800° C. to some extent. | Readily decomposed (180° C.). |
| Effect of oxidising agents. | Not affected. | Permanganates, dichromates, nitric acid, lead dioxide, manganese dioxide, oxidise it to chlorine and water. | Those mentioned under HCl and also hydrogen peroxide, chlorine and sulphuric acid oxidise it to bromine and water. | All oxidising agents, including the above, and also nitrous acid, ferric and cupric salts and bromine oxidise it to iodine and water. |

# CHAPTER XXIII

## MANGANESE AND THE ELEMENTS OF GROUP VII. A

THIS group, VII. A of the Periodic table, contains manganese and two other very rare elements, technetium and rhenium, which were discovered only during the last few years. Potassium perrhenate is now commercially obtainable, but technetium has not been obtained in weighable quantities.

The atomic structure of these three elements is given below.

| Element. | Electrons of | | | | | |
|---|---|---|---|---|---|---|
| | 1 quantum. | 2 quanta. | 3 quanta. | 4 quanta. | 5 quanta. | 6 quanta. |
| Manganese . . | 2 | 8 | (8, 5) | 2 | | |
| Technetium . . | 2 | 8 | 18 | (8, 6) | 1 | |
| Rhenium . . | 2 | 8 | 18 | 32 | (8, 5) | 2 |

The chemical properties of technetium are not yet known, but manganese and rhenium are characterised by highly variable valency. Both elements form four or five oxides, several of which are acidic in character and form stable per-salts, permanganates and per-rhenates analogous to the perchlorates. In the existence of these salts and in the existence and properties of the heptoxides, $Mn_2O_7$, $Re_2O_7$, the only resemblance of these elements to the halogens resides.

### MANGANESE Mn, 54·93

**1106. Occurrence.**—The chief ore of manganese is *pyrolusite* manganese dioxide $MnO_2$. It occurs also as the sesquioxide $Mn_2O_3$, trimanganic tetroxide $Mn_3O_4$, and as sulphide, carbonate and silicate in other minerals.

**1107. Preparation.**—Manganese is now prepared in a high degree of purity by the electrolysis of manganous sulphate solutions. The ore is reduced to the crude metal or manganous oxide with carbon in an electric furnace, and then extracted with spent electrolyte, chiefly ammonium sulphate solution. Iron and arsenic are precipitated from the resultant solution by the addition of ammonia, whilst nickel and cobalt are removed with ammonium sulphide.

The filtrate, consisting of manganese and ammonium sulphates, is then electrolysed, using stainless steel cathodes and lead anodes. Finally the manganese is stripped from the steel cathodes and the spent electrolyte is used to leach more of the reduced ore.

**1108. Properties.**—Pure manganese is a soft grey metal. Its density is 7·2 and its specific heat 0·107. It melts at 1,245° C.

Manganese burns in air if finely divided. It is attacked by chlorine and sulphur. When heated in nitrogen it forms nitrides.

Manganese, if it contains any carbon, is readily attacked by water or moist air,

$$Mn_3C + 6H_2O = 3Mn(OH)_2 + CH_4 + H_2$$
$$Mn + 2H_2O = Mn(OH)_2 + H_2.$$

Pure manganese as obtained by electrolysis is not attacked by pure water and only slightly by steam.

Manganese is attacked by acids, both dilute and concentrated, and behaves normally in this respect.

Pure manganese has no industrial uses, but the metal forms valuable alloys. Ordinary steel contains a proportion of manganese, from 0·1 to 0·3 per cent. being usual quantities. Cast iron contains up to 2 per cent. The presence of manganese in steel improves its strength and its working qualities. 'Manganese steel' contains as much as 10 per cent. of manganese and is very hard without being brittle, and also more resistant to corrosion than ordinary steel. It is employed for tram-line points and other articles which must sustain heavy wear and violent shocks.

When 3 per cent. of manganese is added to brass the tensile strength of this alloy is increased so as to equal that of mild steel. When added to magnesium and aluminium, it also increases their strength and enhances their resistance to corrosion, as in Dural (§ 481).

*Atomic Weight of Manganese.*—The atomic weight of this element is shown by Dulong and Petit's law to be about 59. The exact value has been obtained by analysis of silver permanganate and by converting manganous chloride and bromide into the corresponding silver compounds. The value 54·93 has been adopted.

**1109. Oxides of Manganese.**—Manganese is an element of very variable valency and presents a formidable array of oxides. These include :—

| | |
|---|---|
| Manganous oxide . . . . | $MnO$ |
| Trimanganese tetroxide . . . | $Mn_3O_4$ |
| Manganese sesquioxide . . . | $Mn_2O_3$ |
| „ dioxide . . . . | $MnO_2$ |
| „ trioxide . . . . | $MnO_3$ |
| „ heptoxide . . . . | $Mn_2O_7$ |

**1110. Manganous Oxide MnO** is best prepared by reducing any other oxide in a current of hydrogen,

$$MnO_2 + H_2 = MnO + H_2O.$$

It is olive-green in colour and is very readily oxidised to trimanganic tetroxide or manganese sesquioxide. It is basic and readily forms manganous salts with acids.

*Manganous hydroxide* $Mn(OH)_2$ is white. It is prepared by the action of alkalis on manganous salts,

$$Mn^{++} + 2OH^- \rightarrow Mn(OH)_2.$$

The air or any oxidising agent converts it into the brown hydrated sesquioxide,

$$2Mn(OH)_2 + O = 2MnO(OH) + H_2O.$$

which occurs native as *manganite*.

**1111. Trimanganese Tetroxide $Mn_3O_4$** occurs native as *hausmannite*. It is made by heating any oxide of manganese strongly in air,

$$6MnO + O_2 = 2Mn_3O_4$$

$$3MnO_2 = Mn_3O_4 + O_2.$$

It dissolves in acids, yielding both manganous and manganic salts or manganous salts and manganese dioxide. With hydrochloric acid it yields chlorine.

**1112. Manganese Sesquioxide $Mn_2O_3$** occurs native as *braunite*. It may be made by the action of chlorine on an excess of manganous carbonate suspended in water,

$$3MnCO_3 + Cl_2 = Mn_2O_3 + MnCl_2 + 3CO_2.$$

The excess of manganese carbonate is removed by treatment with dilute nitric acid, which only affects the sesquioxide very slowly.

Manganese sesquioxide is a brown powder. Dilute acids slowly convert it into manganic salts (*q.v.*). These may decompose, giving manganese dioxide.

On warming the oxide with hydrochloric acid chlorine is formed,

$$Mn_2O_3 + 6HCl = 2MnCl_3 + 3H_2O$$
$$2MnCl_3 = 2MnCl_2 + Cl_2.$$

*Manganic hydroxide* $Mn(OH)_3$ does not seem to exist, but the hydrated sesquioxide $MnO(OH)$ or $Mn_2O_3 . H_2O$ is a native mineral.

**1113. Manganese Dioxide $MnO_2$.**—This oxide—the most important compound of manganese—occurs native. The mineral *pyrolusite* is a hard black crystalline variety. *Psilomelane* is a hydrated form, usually containing barium, $\left.\begin{matrix}MnO\\BaO\end{matrix}\right\}MnO_2\ aq.$ *Wad* is an earthy brownish-black variety, and is less pure than the others.

Since native pyrolusite is nearly pure manganese dioxide, it is not necessary to prepare manganese dioxide on the commercial scale.

In the laboratory it may be made by heating the nitrate to *ca.* 200° C. and extracting the residue with nitric acid, which does not attack manganese dioxide. The residue is well washed and dried,

$$Mn(NO_3)_2 = MnO_2 + 2NO_2.$$

Manganese dioxide forms a black powder, insoluble in water.

When heated to strong redness, it decomposes, yielding triman-

ganic tetroxide and oxygen—an obsolete method of preparing the latter gas,

$$3MnO_2 = Mn_3O_4 + O_2.$$

Dilute acids do not attack it, except hydrochloric acid which, when moderately dilute, evolves chlorine. Concentrated hydrochloric acid attacks the oxide, probably forming manganese tetrachloride, which decomposes slowly in the cold and rapidly on warming to form manganic chloride and chlorine. The trichloride decomposes on further heating into manganous chloride and chlorine,

$$MnO_2 + 4HCl \rightleftharpoons MnCl_4 + 2H_2O$$
$$2MnCl_4 \rightleftharpoons 2MnCl_3 + Cl_2.$$
$$2MnCl_3 \rightleftharpoons 2MnCl_2 + Cl_2$$

Nitric acid does not affect it, but concentrated sulphuric acid on heating produces manganous sulphate and oyxgen,

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

Probably, in the cold, a sulphate, $Mn(SO_4)_2$, is produced.

Manganese dioxide is sometimes called manganese peroxide, but it is not a peroxide in the true sense, as are, for example, barium or sodium peroxides. It is not a salt of hydrogen peroxide, but a basic oxide which with acids forms highly unstable salts.

Manganese dioxide is an oxidising agent, a property displayed in its action on hydrochloric acid. If boiled with dilute sulphuric acid and oxalic acid it oxidises the latter to carbon dioxide,

$$H_2C_2O_4 + MnO_2 + H_2SO_4 = 2H_2O + 2CO_2 + MnSO_4.$$

The proportion of manganese dioxide in a sample may be determined by heating a known weight with a known volume of standard oxalic acid and sulphuric acid, then determining the excess of oxalic acid with permanganate.

It finds its chief uses in the manufacture of chlorine (*q.v.*), in the decolorising of glass and in the manufacture of Leclanché batteries. When added to a charge of molten glass, which would without such addition give a green-tinted product as a result of the presence of ferrous silicate derived from iron in the sand used, it oxidises this to ferric silicate, which is much paler in colour, while the pinkish tint given by manganese to glass neutralises the greenish tint due to iron. The purplish tint often noticeable in old glass is said to be due to the slow oxidation of green ferrous silicate, causing the violet colour of the added manganese to become apparent.

Manganese, in small quantities, colours glass and pottery glazes amethyst purple ; when more is used it gives a good black.

**1114. Manganese Trioxide $MnO_3$.**—This very peculiar compound is formed when potassium permanganate is dissolved in *cold* concentrated sul-

phuric acid and the solution dropped on to anhydrous sodium carbonate. Pinkish-purple clouds are produced which may be condensed in cooled U-tubes.

It is a reddish, volatile and deliquescent solid, irritating to the throat and lungs. It dissolves in water, forming manganese dioxide and permanganic acid. With alkalis it gives manganates,

$$2NaOH + MnO_3 = Na_2MnO_4 + H_2O.$$

It is therefore an acidic oxide.

**1115. Manganese Heptoxide $Mn_2O_7$** is formed by the action of sulphuric acid on potassium permanganate. If concentrated sulphuric acid be used the oxide dissolves in the excess of acid, forming the compound $(MnO_3)_2SO_4$, but if potassium permanganate be added slowly to well-cooled sulphuric acid of the composition $H_2SO_4 . H_2O$ (d. 1·78), the oxide separates in oily drops. It has been distilled in very small quantity and forms a purple vapour.

Manganese heptoxide forms a reddish-brown oil with a chlorine-like odour. When warmed, it decomposes suddenly with a slight explosion, giving flakes of manganese dioxide and evolving oxygen,

$$2Mn_2O_7 = 4MnO_2 + 3O_2.$$

With water it gives permanganic acid,

$$H_2O + Mn_2O_7 = 2HMnO_4.$$

It is a very powerful oxidising agent, inflaming wood or paper when dropped upon them.

**1116. Oxyacids of Manganese and their Salts.**—There are three series of salts derived from manganese oxyacids, real or hypothetical.

| | |
|---|---|
| (Manganous acid), manganites . . | $X_2'MnO_3$ |
| (Manganic acid), manganates . . | $X_2'MnO_4$ |
| Permanganic acid, permanganates . | $X'MnO_4$ |

**1117. Manganites.**—When manganese dioxide, particularly when hydrated is treated with alkalis it forms substances known as *manganites*. It is very probable that these are only colloidal solutions or mixtures.

The so-called calcium manganite finds a use in the Weldon process for recovery of manganese dioxide from chlorine residues (*v.* § 1042).

Potassium manganites are considered to be formed when manganese dioxide is heated with caustic potash. If air is present they oxidise to the manganate (*q.v.*).

**1118. Manganates.**—Manganic acid does not exist, but potassium manganate $K_2MnO_4$ is formed when manganese dioxide is fused with caustic potash, potassium nitrate being added as a rule, in order to supply oxygen. The process is usually performed in a flat shallow vessel to allow as free an access of air as possible,

$$2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O.$$

The mass is extracted with water and gives a deep green solution from which green crystals may be obtained by evaporation.

The action of even feeble acids causes the salt to be converted into the permanganate and manganese dioxide. The colour of the

solution changes from green to pink and the manganate has been fancifully termed the ' mineral chameleon.'

$$3K_2MnO_4 + 2CO_2 = 2K_2CO_3 + 2KMnO_4 + MnO_2$$

*or* $$3MnO_4^{--} + 4H^+ = 2MnO_4^- + 2H_2O + MnO_2.$$

The manganates are powerful oxidising agents, and in general behave in a similar manner to the permanganates. The general equation for their oxidising action is

$$H_2O + K_2MnO_4 = 2KOH + MnO_2 \downarrow + O,$$

hydrated manganese dioxide being deposited as a brown precipitate. They are little used as oxidising agents, the permanganates being preferable.

*Sodium manganate* $Na_2MnO_4$ is contained in Condy's fluid together with the permanganate. To make the fluid crude caustic soda is fused with manganese dioxide at a low red heat in a shallow vessel for about forty-eight hours. The mass is extracted with water and concentrated by evaporation.

**1119. Permanganic Acid $HMnO_4$.**—This acid is made from potassium permanganate. Concentrated silver nitrate solution and concentrated potassium permanganate solution are mixed in equivalent proportions, when a red precipitate of silver permanganate results,

$$Ag^+ + MnO_4^- \rightarrow AgMnO_4.$$

This is filtered off through glass wool and washed with a little water. It is then dissolved in much water and barium chloride is added till no further precipitate is given,

$$BaCl_2 + 2AgMnO_4 = Ba(MnO_4)_2 + 2AgCl \downarrow .$$

The silver chloride is filtered off and to the solution of barium permanganate sulphuric acid is added as long as a precipitate is produced,

$$Ba(MnO_4)_2 + H_2SO_4 = BaSO_4 + 2HMnO_4.$$

The barium sulphate is allowed to settle out or is removed by filtration through an asbestos mat, and the solution of permanganic acid is evaporated cautiously.

Permanganic acid is a brown crystalline solid, which dissolves in water to form a pink or violet solution, which has all the oxidising properties of the permanganates described below.

Its solution decomposes when heated, giving manganese dioxide and oxygen,

$$4HMnO_4 = 2H_2O + 4MnO_2 + 3O_2.$$

**1120. Potassium Permanganate $KMnO_4$.**—This salt, which is of the greatest value as an oxidising agent in chemical work, is made,

as a rule, by preparing the manganate as described above and adding to it dilute sulphuric acid or passing carbon dioxide,

$$3K_2MnO_4 + 2H_2SO_4 = 2K_2SO_4 + 2KMnO_4 + MnO_2 + 2H_2O.$$

*or*
$$3MnO_4{}^{--} + 4H^+ = 2MnO_4{}^- + 2H_2O + MnO_2.$$

The solution is decanted from the hydrated manganese dioxide and evaporated. The permanganate being sparingly soluble (*c.* 4 per cent. at room temperature) crystallises before the sulphate.

On the laboratory scale, 10 grams of potassium hydroxide may be ground with 5 gms. of potassium chlorate and melted in an iron or nickel vessel; 10 gms. of manganese dioxide are stirred into the liquid with an iron rod. Heating is continued until the mass becomes dry, finally bringing the crucible to a low red heat.

$$2KOH + 2MnO_2 + KClO_3 = 2KMnO_4 + H_2O + KCl.$$

The solid is boiled with much water and saturated with carbon dioxide until a drop on filter paper shows no green colour. The solution is then decanted from unchanged manganese dioxide, etc., filtered through glass wool, evaporated till crystals begin to form, decanted while hot from any precipitate and left to crystallise.

Potassium permanganate forms dark purple crystals which appear greenish by reflected light. The crystals are isomorphous with those of potassium perchlorate. It is not very soluble in water, 6·45 gms. dissolving in 100 gms. water at 15° C.

Potassium permanganate is decomposed, when strongly heated, to the manganate, manganese dioxide and oxygen,

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

When treated with concentrated sulphuric acid it gives manganese heptoxide, which may decompose explosively,

$$2KMnO_4 + H_2SO_4 = Mn_2O_7 + K_2SO_4 + H_2O$$
$$(2Mn_2O_7 = 4MnO_2 + 3O_2).$$

Potassium permanganate is, both in the solid state and in solution, a powerful oxidising agent.

Heated in hydrogen the crystals burn, giving manganous oxide and caustic potash,

$$2KMnO_4 + 5H_2 = 2KOH + 2MnO + 4H_2O.$$

When rubbed or heated with sulphur or phosphorus it explodes, and mixture of permanganates with organic matter may ignite spontaneously or explode when rubbed or heated. In this respect it shows its resemblance to potassium perchlorate.

In solution it is the most powerful common oxidising agent available.

In absence of acids the general equation for its oxidation of other substances ($X$) is

$$2KMnO_4 + H_2O + 3X = 2KOH + 2MnO_2 + 3XO$$

*or* $$2MnO_4^- + 3X + H_2O = 2OH^- + 2MnO_2 + 3XO.$$

Caustic potash and brown hydrated manganese dioxide (often mixed with the sesquioxide) are the products.

In strongly alkaline solution the manganate is formed, only *one* atom of oxygen becoming available,

$$2KMnO_4 + 2KOH + X = 2K_2MnO_4 + H_2O + XO.$$

In presence of acids (sulphuric acid is normally used for the purpose) the reaction is,

$$2KMnO_4 + 4H_2SO_4 + 5X = 2KHSO_4 + 3H_2O + 2MnSO_4 + 5XO,$$

*or* $$2MnO_4^- + 6H^+ + 5X = 2Mn^{++} + 3H_2O + 5XO.$$

manganous and potassium salts being formed.

The substances oxidised include nascent hydrogen, unsaturated hydrocarbons, ammonia[1] and ammonium salts, nitrites, hydrogen sulphide, sulphur dioxide, sulphites, thiosulphates, phosphine, phosphites, hypophosphites, phosphorous acid, hydrochloric acid, chlorides, hydrobromic and hydriodic acid and their salts, arsenites, organic matter of most kinds, the lower salts of most metals, such as ferrous, cuprous, manganous, titanous, stannous salts and metals. The equations for most of these reactions are given under the headings of the particular compound, but they are readily obtained by writing the equation for the reaction of the compound with the appropriate amount of oxygen and adding this to the general equation for the reaction of permanganate with oxidising agents. Thus, if we require the equation for the reaction of acid potassium permanganate with ferrous sulphate we first write,

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O$$

and then

$$10FeSO_4 + 5H_2SO_4 + 5O = 5Fe_2(SO_4)_3 + 5H_2O.$$

By adding this to

$$2KMnO_4 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 3H_2O + 5O$$

and eliminating what is identical (5O) on each side of the resulting equation, we have

$$10FeSO_4 + 2KMnO_4 + 9H_2SO_4 = 5Fe_2(SO_4)_3 + 2KHSO_4 + 2MnSO_4 + 8H_2O.$$

[1] Only slowly in solution.

Again, consider its reaction with sulphur dioxide,

$$5SO_2 + 5O + 5H_2O = 5H_2SO_4$$
$$2KMnO_4 + 4H_2SO_4 = 2KHSO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$2KMnO_4 + 5SO_2 + 2H_2O = H_2SO_4 + 2KHSO_4 + 2MnSO_4.$$

In this case the equation shows us that no addition of sulphuric acid is necessary to bring about the oxidation of sulphur dioxide with the simultaneous formation of manganous and potassium salts.

If we require the equation for the reaction of neutral permanganate a similar process may be used. Suppose we require the reaction of ammonia with potassium permanganate. We have

$$2NH_3 + 3O = N_2 + 3H_2O$$
$$2KMnO_4 + H_2O = 2KOH + 2MnO_2 + 3O$$
$$2KMnO_4 + 2NH_3 = N_2 + 2KOH + 2MnO_2 + 2H_2O.$$

The use of the ionic equations is often simpler. Suppose we require the reaction of acid potassium permanganate with a nitrite. We have

$$5NO_2^- + 5O = 5NO_3^-$$
$$2MnO_4^- + 6H^+ = 2Mn^{++} + 3H_2O + 5O$$
$$2MnO_4^- + 5NO_2^- + 6H^+ = 5NO_3^- + 2Mn^{++} + 3H_2O.$$

The correct writing of these equations is most important in view of the extended use of potassium permanganate as an oxidising agent in volumetric analysis. The reaction of potassium permanganate with hydrogen peroxide is of interest. It is discussed in § 214 (cf. also p. 605).

The analytical use of acid potassium permanganate solution depends on the fact that its reduction products are almost colourless. Thus, on adding a standard solution of potassium permanganate to an acidified solution of a reducing agent its intense purple colour at once disappears until all the reducing agent has been oxidised. The next drop of the permanganate marks the end-point by colouring the solution pink. The method has been used for the determination of ferrous iron, oxalic acid, sulphites, nitrites, hydrogen peroxide, etc.

Alkaline or neutral potassium permanganate is reduced to a greater extent than the general equation indicates by the action of such powerful reducing agents as hydrogen sulphide and potassium iodide. The manganese dioxide formed is a powerful enough oxidising agent to react with these, being thereby reduced to some compound of tervalent or bivalent manganese.

Potassium permanganate attacks and oxidises most of the metals.

**1121. Manganese Salts.**—Manganese forms one stable series of salts, the manganous salts in which the metal is divalent. There are also trivalent salts, which are unstable.

**1122. General Properties of Manganous Salts.**—Manganous salts are in general pink in colour and in solution furnish the manganous ion, $Mn^{++}$. The solutions are of a pale pink tinge. Solutions of manganous salts give, with alkalis, a white precipitate of manganous hydroxide, which soon turns brown as a result of oxidation by the air.

Manganous salts also give a pink precipitate of manganous sulphide MnS with hydrogen sulphide, provided acids are not present.

Oxidising agents in alkaline solution convert them into brown hydrated manganese dioxide usually mixed with some of the sesquioxide. Thus sodium hypochlorite oxidises them in this way,

$$NaOCl + Mn(OH)_2 = NaCl + MnO_2 + H_2O.$$

Oxidation to permanganate occurs if an excess of the hypochlorite is used and heat is applied. If boiled with lead dioxide (or better, red lead) and nitric acid, they form permanganic acid.

**1123. Manganous Carbonate $MnCO_3$.**—This salt is obtained by the action of sodium carbonate solution on a manganous salt. It forms a pinkish-buff powder, which has the general properties of carbonates.

When heated in air it gives manganous oxide, which at once oxidises to manganese dioxide,

$$MnCO_3 = MnO + CO_2$$
$$2MnO + O_2 = 2MnO_2.$$

**1124. Manganous Nitrate $Mn(NO_3)_2$** is readily prepared by the usual methods, such as the action of nitric acid on the carbonate. It is a very soluble pink salt. When ignited it leaves, not manganous oxide, but manganese dioxide,

$$Mn(NO_3)_2 = MnO_2 + 2NO_2.$$

This is the best method for preparing pure manganese dioxide.

**1125. Manganous Sulphide MnS** is formed as a pale pink or buff precipitate by the action of hydrogen sulphide on a neutral or alkaline solution of a manganese salt.

It is readily soluble in acids, giving a manganous salt and hydrogen sulphide.

**1126. Manganous Sulphate $MnSO_4$** is prepared commercially by heating a semi-solid mixture of manganese dioxide and sulphuric acid,

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

It is recrystallised from water. The ordinary methods of preparing sulphates may also be used on the laboratory scale with more convenience.

Manganous sulphate forms pink triclinic crystals with 5 molecules of water of crystallisation, which are isomorphous with copper sulphate. It has the usual properties of sulphates and manganous salts.

**1127. Manganous Chloride $MnCl_2 . 4H_2O$.**—This salt is readily obtained by boiling manganese dioxide with hydrochloric acid till the steam contains no chlorine. The solution so obtained usually contains iron, and this may be removed by adding enough ammonia to cause a slight precipitate, boiling and filtering. Iron and a little manganese are precipitated as hydroxides. The solution on evaporation yields rose-pink crystals of manganous chloride.

Manganous chloride is deliquescent and very soluble in water, 100 gms. of which dissolve 77·2 gms. of the anhydrous salt at 25° C. The salt finds a use in the curious process of dyeing cotton *manganese-brown*. The cotton is soaked in manganous chloride and passed through weak caustic soda. Manganous hydroxide is precipitated on the fibre and is oxidised on drying to brown higher oxides.

*Manganous borate* and *oxalate* are used as 'driers' in oil paint.

**1128. Manganic Salts.**—These salts, in which manganese is trivalent, are markedly unstable. The brown solution formed when manganese dioxide is dissolved in hydrochloric acid (§ 1113) is believed to contain manganese trichloride $MnCl_3$, and probably manganese tetrachloride $MnCl_4$. Double salts of these with alkali chlorides have been made.

*Manganic sulphate* $Mn_2(SO_4)_3$ is obtained by the action of sulphuric acid on freshly-precipitated manganese dioxide or sesquioxide. It forms a green solid. If crystallised with potassium sulphate, potassium manganese alum $K_2SO_4 . Mn_2(SO_4)_3 . 24H_2O$ is formed. This salt is somewhat unstable in solution, readily precipitating hydrated manganese dioxide.

**1129. Detection and Estimation of Manganese.**—The best special test for manganese is the reaction described in § 1118.

A piece of potash and a crystal of potassium nitrate are mixed with a drop of the solution or a few grains of the solid to be tested, and fused on a piece of porcelain. The formation of a dark green mass, dissolving in a little water to form a green solution of manganate, which becomes pink on the addition of dilute sulphuric acid, indicates the presence of manganese.

**Manganese may be precipitated as manganese ammonium phosphate, ignited, and weighed as the pyrophosphate $Mn_2P_2O_7$. Alternatively it may be determined as sulphide MnS.**

Manganese may be estimated volumetrically by several methods, the best of which is to titrate a hot manganous salt containing an excess of zinc salts and some zinc oxide with potassium permanganate. The reaction results in the formation,

$$3MnSO_4 + 2KMnO_4 + 2H_2O + 5ZnO = 5ZnO \,.\, MnO_2 + K_2SO_4 + 2H_2SO_4,$$

of insoluble zinc manganite. The end-point is marked by the supernatant liquid becoming red.

The method of oxidation to permanganate by sodium bismuthate and nitric acid has been described in § 836.

## TECHNETIUM AND RHENIUM

**1130. Discovery.**—In the year 1925, Noddack, Berg and Tacke[1] decided that as platinum ore and columbite (§ 850) both contained a number of the elements which surrounded the spaces in the Periodic table corresponding to eka- and dwi-manganese, these latter elements might well be present in these minerals. The minerals were treated in such a way as to concentrate any elements resembling manganese, and lines in the X-ray spectra indicated the presence of elements of atomic weight corresponding to spaces 43 and 75 in the Periodic table. The lighter of these elements was named masurium (from a district in Prussia), and the heavier, rhenium (from the German Rhine).

The discovery of masurium has not been confirmed but an artificial radioactive element, now named *technetium*, discovered by Mlle. Percy in 1939, fills the gap.

### TECHNETIUM Tc Isotopes 96,99

This element occurs in the fission products of uranium 235 and can also be made by bombarding molybdenum with neutrons. The isotope obtained from uranium, Tc 99, is fairly stable, decaying by a $\beta$-ray change to ruthenium (half-period $4 \times 10^6$ yr.). Its chemical properties have not been investigated.

### RHENIUM Re, 186·31

*Occurrence.*—Rhenium is present in many minerals, notably molybdenite and pyrolusite. The richest minerals contain up to four parts of rhenium per million.

I. and W. Noddack started with more than half a ton of molybdenite (§ 1005). They precipitated nearly all the molybdonum from the solution obtained from it as ammonium phospho-molybdate (§ 785). The residue, after further treatment, was converted into oxides and fused with sodium hydroxide and sodium nitrate. Most metals present were unaffected but the rhenium formed sodium perrhenate $NaReO_4$. This was reduced with hydrogen sulphide to a sulphide containing 1·9 per cent. of rhenium. This was reduced to metal in a current of hydrogen and then heated in oxygen at 150° C. The volatile oxide $Re_2O_7$ distilled over and when reduced gave fairly pure rhenium. This was further purified by similar methods, and 1 gm. of pure rhenium was obtained. Potassium perrhenate is now commercially obtainable.

[1]Now Fr. Ida Noddack.

**1131. Rhenium and Its Compounds.**—Rhenium is a grey metal of very high density (21·4). It has an exceedingly high melting point, 3,167° C. It is readily oxidised to a volatile oxide, $Re_2O_7$.

*The oxides of rhenium* are many. $ReO_2$, $ReO_3$, $Re_2O_7$, are known, and lower oxides have been reported. $ReO_2$ seems to be analogous to manganese dioxide. $Re_2O_7$ is a fusible and volatile solid which, unlike manganese heptoxide, is stable. It dissolves in water, forming perrhenic acid $HReO_4$. The perrhenates are the best-known compounds of rhenium. They are colourless, in contrast to the permanganates, and are much less powerful oxidising agents than these.

*Rhenium chloride* $ReCl_4$ is the most readily prepared, but $ReCl_5$ is also known. A fluoride $ReF_6$ has been prepared. These halides are not true salts and are hydrolysed by water. $ReCl_4$ is obtained from manganese salts by removing manganese with ammonium sulphide and traces of calcium as oxalate, when the small quantity of rhenium remaining may be obtained as chloride.

*Rhenium sulphides* $ReS_2$ and $Re_2S_7$ are typical of the element. Both are black.

*Salts of rhenium* are probably contained in solutions obtained by electrolytic reduction of perrhenates.

# CHAPTER XXIV

## IRON, COBALT, NICKEL, AND THE PLATINUM METALS

**1132. Group VIII. of the Periodic Table.**—Group VIII. in the Periodic table of Mendeléeff differs from the others in containing three sets each of three elements.

| | | |
|---|---|---|
| Iron | Cobalt | Nickel. |
| Ruthenium | Rhodium | Palladium. |
| Osmium | Iridium | Platinum. |

The three elements of each horizontal and vertical set resemble each other closely, and there is a general resemblance perceptible throughout the whole group. These elements are the central ones of the transition elements of the three long periods, and should be looked on as making the series of elements continuous from Group VII. A to Group I. B. Thus the series :—

*Chromium*, *manganese*, iron, cobalt, nickel, *copper*, *zinc*, shows a steady gradation of properties, as do also

*Molybdenum* . . . ruthenium, rhodium, palladium, *silver*, *cadmium*; and *tungsten*, *rhenium*, osmium, iridium, platinum, *gold*, *mercury*.

The general likeness of the sets (*a*), (*b*), (*c*) above is chiefly to be noticed in the following particulars : Characteristic of the group is the high melting point of the metals, from 1,400° C. upwards, and also the catalytic properties of the metals. They are all of variable valency and show a remarkable tendency to form stable complex compounds with other elements and groups. The ferrocyanides are paralleled by palladocyanides or platinocyanides. Cobaltammines and platinammines are also examples of this complex formation.

**1133. Iron, Cobalt and Nickel.**—Iron, nickel and cobalt show numerous points of resemblance. The metals are fairly hard and fuse at high temperatures. They are decidedly para-magnetic, iron being by far the most magnetic metal, nickel and cobalt much less magnetic than iron, but a great deal more magnetic than any other element. They are, moreover, not only strongly para-magnetic, but *ferro-magnetic*, *i.e.*, they are capable of acting as magnets. They are all three of variable valency. Their salts are isomorphous. All three elements (together with the remainder of those in Group VIII.) show a remarkable tendency to form complex compounds (ferro-

cyanides, ferrioxalates, cobaltinitrites, cobalticyanides, nickelicyanides, etc.).

The elements all form volatile carbonyls (§§ 1172, 1217).

Their atomic structure is indicated in the table :—

| Elements. | Electrons of | | | |
|---|---|---|---|---|
| | 1 quantum. | 2 quanta. | 3 quanta. | 4 quanta. |
| Iron . . | 2 | 8 | 8, 6 | 2 |
| Cobalt . . | 2 | 8 | 8, 7 | 2 |
| Nickel . . | 2 | 8 | 8, 8 | 2 |

Their likeness is occasioned by the fact that they have each two electrons in the outer valency group, but the neighbouring elements also share this resemblance. It is certainly doubtful whether, apart from the necessities of Mendeléeff's grouping, we should ever have drawn any line separating any particular three elements in the sequence : chromium, manganese, iron, cobalt, nickel, copper.

## IRON Fe, 55·84

**1134. Historical.**—Iron has been known from very early times (*c.* 3000 B.C.), for it occurs native as meteoric iron. The date at which the manufacture of iron first began is hard to fix, but doubtless it was coming into prominence from *c.* 1500 B.C. onward. In Homer's time, *c.* 1200 B.C., iron was looked on as a valuable, if not precious, metal :—

> *νῦν δ' ὧδε ξὺν νηὶ κατήλυθον ἠδ' ἑτάροισι*
> *πλέων ἐπὶ οἴνοπα πόντον ἐπ' ἀλλοθρόους ἀνθρώπους*
> *ἐς Τεμέσην μετὰ χαλκόν, ἄγω δ' αἴθωνα σίδηρον.*
>
> (ODYSSEY I., 182).

("But now I have touched here with ship and men, sailing on the wine-dark sea to peoples of foreign speech to Temese[1] for bronze, and I bring with me burnished iron.")

The Romans worked iron, and in the Forest of Dean and also in Sussex the remains of Roman iron-works are to be found. The primitive method of iron working as practised by the Romans was probably the simple building of a stack of charcoal and lumps of ore,

[1] In Cyprus, where copper was extensively mined in antiquity.

igniting this and increasing the temperature by blowing with bellows, a method practised by primitive peoples to-day. Small blast furnaces date from the late Roman period, and were steadily improved up to the early sixteenth century; the seventeenth century saw the substitution of coke for charcoal.

In the eighteenth century the making of wrought iron from cast iron by puddling was discovered. The demand for iron was greatly increased by the development of the steam-engine and of railways. Throughout the late eighteenth and the nineteenth century blast furnaces were increased in size and efficiency. After 1860 the manufacture of low-priced steel gave a further stimulus to production.

**1135. Occurrence of Iron.**—Iron is found native as meteoric iron. Apparently many of the dark bodies which travel through space are composed of iron. These, entering the atmosphere with velocities approximating to twenty miles a second, heat up and burn. The largest may reach the ground unconsumed. They are ordinarily composed of iron with a small proportion of other metals, notably nickel. They contain, moreover, a higher proportion of the platinum metals than does the earth's crust as a whole, a fact which may indicate that elements of high atomic number may be more stable under certain stellar conditions than in the solar system.

There are three chief classes of iron ore :—

(1) *Magnetite* $Fe_3O_4$.—This ore of iron occurs in great quantities in Sweden and in North America on the shores of Lake Superior. It is very pure and furnishes a soft iron of high quality.

(2) *Hæmatite* $Fe_2O_3$. Ferric oxide occurs as a hard reddish-purple mineral, and also in a brown, softer, partly hydrated form. The first type, 'red hæmatite,' is found in Cumberland and also in the United States and in Spain. The brown hæmatites are found in England (in Northamptonshire), France and North Germany, and the United States, and are as a rule much less pure than the red hæmatite. Most of the brown hæmatites contain a good deal of phosphorus, which is injurious to the quality of the iron produced, but their abundance renders them one of the most valuable sources of iron. Iron is a heavy and cheap commodity and it pays better to make it from a poor ore on the spot than from a rich and pure ore a thousand miles from the place where the metal is wanted.

(3) *Carbonate ores.* These are mixtures of ferrous carbonate with clayey material. *Spathic iron ore* is almost pure ferrous carbonate. *Clay ironstone* and *Cleveland ironstone* are mixtures of ferrous carbonate and clay. *Black band ironstone* contains also bituminous material. These ores are of comparatively low purity.

Many minerals besides the above contain iron, and the metal is very widely distributed. It is rare to find any mineral or, indeed,

any natural object whatever which does not contain appreciable traces of the metal.

Iron is contained in all living things. The hæmoglobin of the blood of animals contains iron, and this element is commonly present in the tissues of plants.

**1136. Extraction of Iron from Its Ores.**—This is one of the most important of industries. In principle it consists of the reduction of oxides of iron to the metal by means of carbon :—

$$(a)\ Fe_2O_3 + 3C = 2Fe + 3CO.$$
$$(b)\ Fe_3O_4 + 4C = 3Fe + 4CO.$$
$$(c)\ FeCO_3 = FeO + CO_2$$
$$FeO + C = Fe + CO.$$

In practice provision must be made—

(1) for continuous working ;

(2) for removal of the ' gangue ' or earthy impurities mixed with the ore.

(3) for removal of some of the sulphur and phosphorus in the ore, if these are present.

**1137. The Blast Furnace** has been evolved through some three

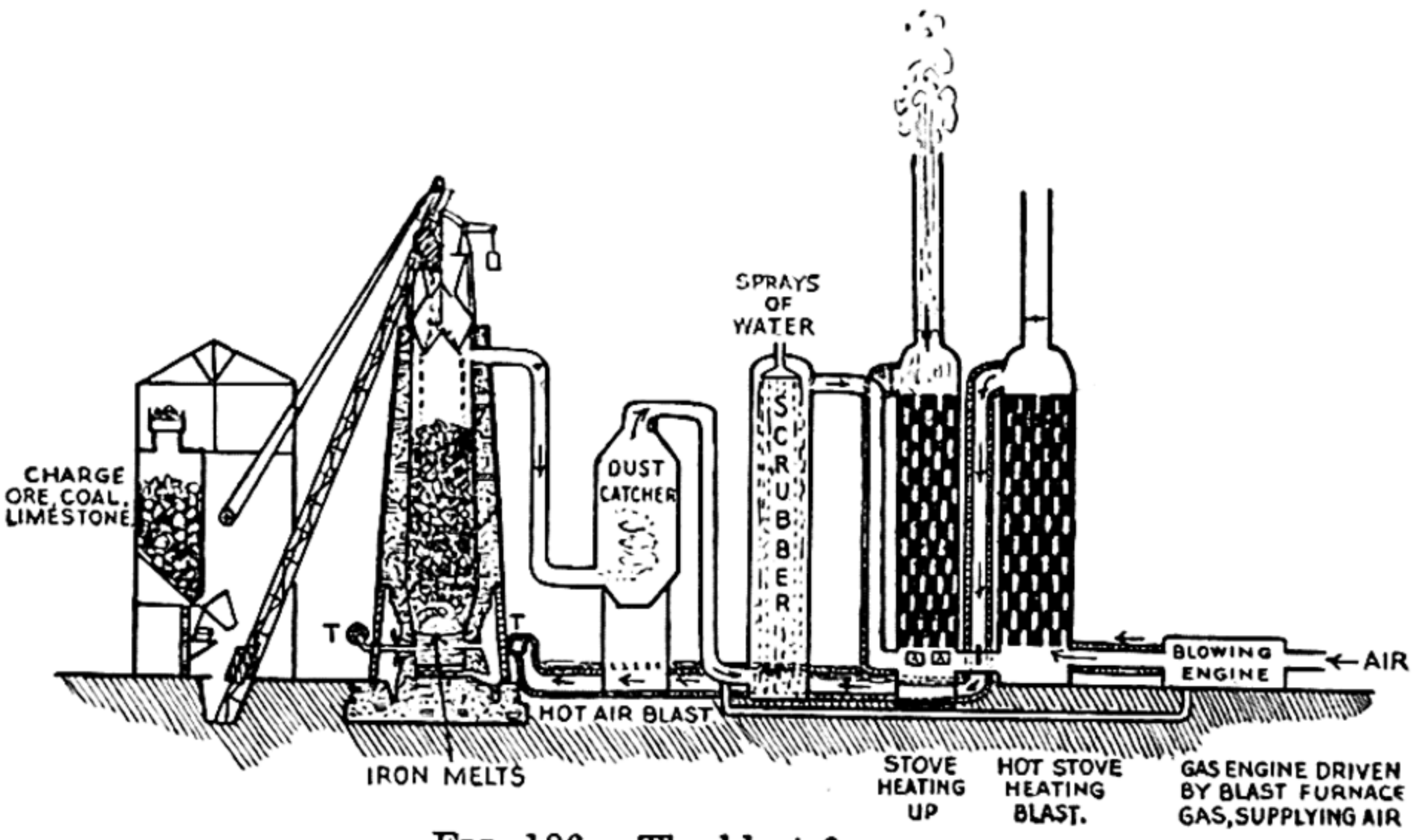



FIG. 186.—The blast furnace.

hundred years and is now always used for the preparation of the impure ' pig iron ' from the ore.

The ores, unless very pure, may be calcined, *i.e.*, heated to redness before they are sent to the blast furnace. This process removes water, if present, and also sulphur, arsenic, etc. It also reduces the ores to a fine state of division in which they are more readily reduced

in the blast furnace. A kiln like a lime kiln (Figs. 85, 86), may be used, or the ores may be heated in rectangular kilns by blast furnace gas.

*Smelting in the Blast Furnace.* The ore is roughly crushed and mixed with limestone and coke in the proportions determined by the composition of the ore treated. These might be 12 : 3 : 5 in the case of an ordinary ironstone. This material is fed into the top of a *blast furnace* (Fig. 186) which may be 120 feet high and may hold some 2,000 tons of the charge.

The chemical changes which take place during the passage of the ore through the furnace are the following :—

At the top of the furnace the ore becomes red hot and the gases passing up the furnace reduce the ore to metallic iron,

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

The iron does not melt at this stage but forms a spongy red-hot mass. A little further down, the limestone decomposes,

$$CaCO_3 = CaO + CO_2,$$

forming carbon dioxide, which combines with the red-hot coke forming some of the carbon monoxide which reduces the iron,

$$CO_2 + C = 2CO.$$

The materials grow hotter as they descend, and the iron gradually melts while the lime combines with the silica and alumina of the earthy matter of the ore, forming a liquid slag of fusible calcium silicates, and aluminates,

$$CaO + SiO_2 = CaSiO_3$$
$$CaO + Al_2O_3 = Ca(AlO_2)_2.$$

In the lower part of the furnace the coke of the charge burns in the blast of air delivered by the 'twyers,' forming carbon dioxide which is reduced to carbon monoxide by the red-hot coke in the higher parts of the furnace. The heat generated by the combustion finally melts the iron and slag, which form two liquid layers. The lighter slag is tapped off from a point somewhat above the level of the liquid iron, which is run off at intervals from a lower tapping hole into moulds. For economical working it is necessary to conserve the heat and chemical energy available in the excess of carbon monoxide which is generated by the process. This gas is usually scrubbed free from dust and utilised for driving the engines which deliver the blast and also for preheating the blast, thus reducing the quantity of coal required. The blast furnace gas is therefore burnt in stoves packed with a chequer-work of firebrick. When

these stoves are hot the blast is taken through them and carries their heat to the furnace. Three stoves usually are heating up while one is cooling down and thereby heating the blast.

Considerable economy is attained by drying the blast, and this process is now being widely adopted. The average blast of air contains from 20 to 120 lbs. of water per ton of pig iron made. This lowers the working temperature, and in fact uses up valuable heat. The drying is effected by means of silica gel which absorbs up to 20 per cent. of moisture. The gel, made by addition of sodium hydrogen sulphate to sodium silicate solution, is dried and supported on perforated trays through which the blast passes. When it has absorbed a proportion of moisture, this is expelled by heat and the gel used again. A saving of some 10 per cent. of the fuel is said to be effected.

The electric blast furnace has found some favour in countries where electricity is cheap and fuel expensive, for if the heating is done electrically only the amount of carbon required to reduce the iron oxide need be added. Fig. 187 shows such a furnace. The issuing gases are in part returned to the base of the furnace in order to conserve heat and to utilise as much carbon monoxide as possible in reducing iron oxide. The blast does not supply air, for since the heating is done electrically, the presence of air is deleterious. The furnaces are used to some extent for making very pure iron from a pure oxide ore and charcoal.

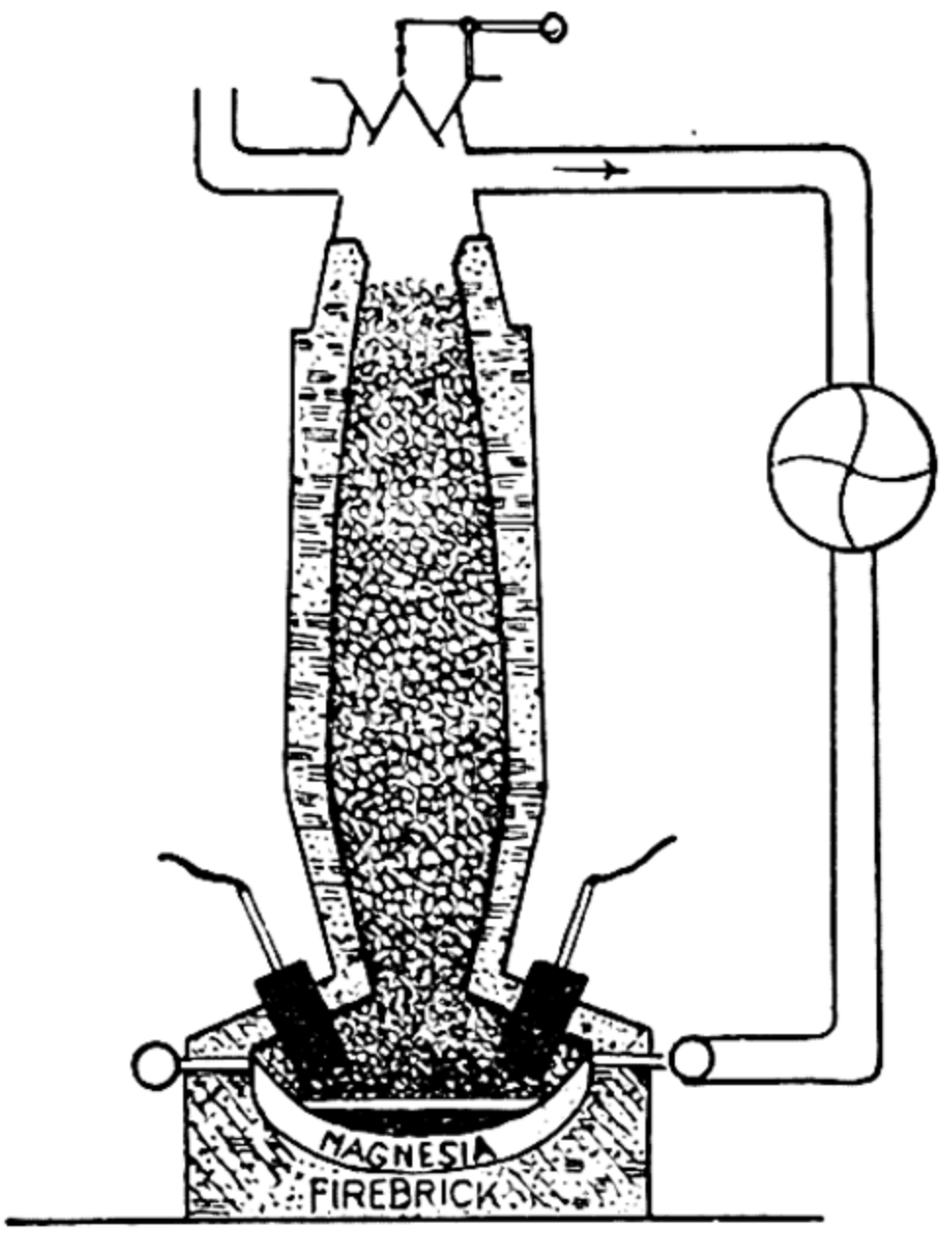



FIG. 187.—Electric blast furnace.

**1138. Cast Iron.**—The iron so obtained is far from pure, usually containing from 1·5 to 4 per cent. of carbon and also smaller quantities of silicon, phosphorus, sulphur, manganese, etc. Cast iron contains, as a rule: Fe, 92 to 95 per cent.; C, 3·5 to 4·3 per cent.; Mn, 0·2 to 1 per cent.; P, 0·5 to 1 per cent.; S, 0·3 to 1 per cent.; Si, 1 to 2 per cent.

The carbon in cast iron is in part combined as iron carbide $Fe_3C$, and in part free as flakes of graphite. Iron containing the latter has a perceptibly grey colour when newly broken.

Iron is required for industrial purposes in three conditions: as cast iron, wrought iron, and steel. Cast iron, of which the manufacture has been already described, is markedly brittle and is not malleable enough to be worked with the hammer either cold or hot. Its compensating advantages are its comparatively low melting

point (*c.* 1,200° C.) and the fluidity of the molten metal. These make it suitable for making castings of all kinds which do not have to withstand great strain or violent shocks. Of the thousands of articles commonly made of cast iron we may instance beds, gutter pipes, fire-grates, lamp-posts, railings, radiators, the bed-plates of most pieces of machinery.

**1139. Wrought iron** is practically pure iron interspersed with 2 to 3 per cent. of slag, and so worked as to have a fibrous structure. It is extremely tough and is easily welded and worked under the smith's hammer. The use of mild steel has largely replaced that of wrought iron.

Wrought iron is prepared by *puddling*, a process which requires a peculiarly skilled and exhausting type of labour for which no satisfactory mechanical substitute has yet been found.

The chief impurities in cast iron are readily oxidisable, and the process of puddling consists of the oxidation of the impurities by means of iron oxide.

A furnace, as illustrated in Fig. 188, has a bed (B) lined with iron oxides in some form, such as hæmatite. A charge of pig iron is placed on this, melted and stirred with long rods, known as rabbles. Silicon and manganese are first oxidised. The temperature is then lowered and the carbon in the metal reacts with the iron oxide of the lining and the iron appears to boil, giving out jets of carbon monoxide,

$$3Fe_3C + Fe_2O_3 = 11Fe + 3CO.$$

A certain amount of slag, mainly ferrous silicate, separates. The phosphorus oxidises at the same time and is eliminated as phosphates

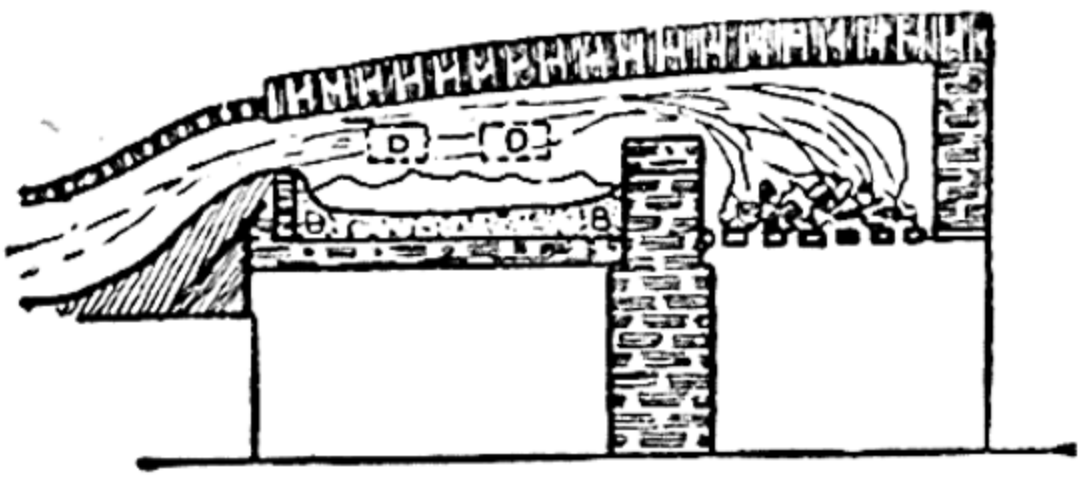



FIG. 188.—Puddling furnace.

in the slag. Pure iron melts at a much higher temperature than cast iron and so, as the latter is purified, it gradually becomes a pasty mass of semi-solid iron mixed with slag. The puddler then, working through the door (D) of the furnace, forms the metal into masses called *blooms*, each weighing rather under a hundredweight. These are hammered and rolled, cut up, reheated and rolled again, so producing wrought iron of characteristic fibrous structure. Puddling is highly skilled labour, calling for great physical strength, and this

fact has led to a decline in the use of wrought iron as compared with mild steel.

Wrought iron, apart from the slag it contains, is nearly pure iron, a typical analysis being : Fe, *c.* 97 per cent. ; slag, *c.* 3 per cent. ; C, 0·02 per cent. ; Mn, 0·005 per cent. ; P, 0·07 per cent. ; S, 0·02 per cent. ; Si, 0·03 per cent.

**1140. Steel.**—The greatest quantity of iron is used in the form of steel, which is iron containing from 0·5 to 1·5 per cent. of carbon, not more than a trace of phosphorus and sulphur (less than 0·1 per cent.) and up to 0·5 per cent. of manganese, and 0·3 per cent. of silicon. Other metals may be added in comparatively large quantities for special purposes, notably, chromium for making stainless steel and manganese, molybdenum, nickel, tungsten and vanadium for various forms of tool steel.

The chief processes for preparing steel are :—

(1) The cementation process. (Production *c.* 200,000 tons per annum.)

(2) The acid and basic converter processes. (Production *c.* 7,500,000 tons per annum.)

(3) Acid and basic open-hearth processes. (Production, *c.* 54,000,000 tons per annum.)

(4) Electrical processes. (Production *c.* 200,000 tons per annum.)

**1141. Cementation Process.**—The oldest process for making steel is the cementation process. In this process good pure wrought iron is cut up into bars, bedded in charcoal and heated for about seven days. The effect of the process is to cause the iron to take up carbon, which probably reaches it as carbon monoxide. The centres of the bars are much less affected than their surfaces, and it is usual to melt and cast the steel so produced to make it uniform in character. The product is the so-called 'crucible steel' used for the finest purposes : shears, razors, and tools of various kinds.

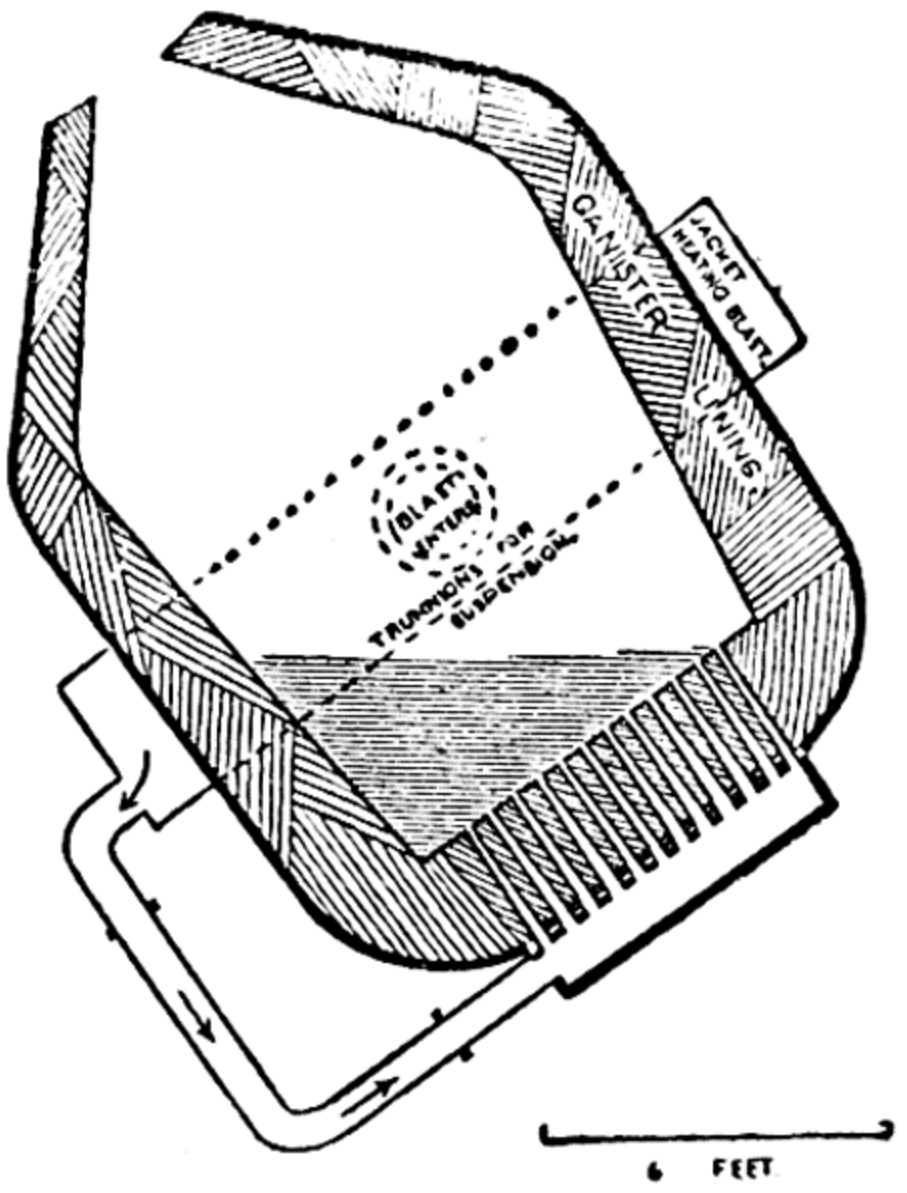



FIG. 189.—Section of Bessemer converter.

**1142. Bessemer Steel.**—The production of steel was enormously simplified by directly oxidising the impurities by a blast of

air forced through the molten pig iron, contained in an egg-shaped vessel known as a *converter* (Fig. 189). The principle of the process depends on the oxidation of carbon to carbon monoxide, and silicon to silica, which forms with the metal a slag of silicate. The phosphorus is more difficult to deal with, and for the original Bessemer process, where the converter is lined with *ganister*, a siliceous material, only pig iron free from phosphorus can be used. Such iron is obtained from most of the red hæmatites.

By lining the converter with a mixture of lime and magnesia mixed with tar to bind it, and by adding lime at the end of the *blow*, phosphorus can be almost completely removed. This is the basis of the Gilchrist-Thomas process. In this process silicon must not be present in large quantities, for the silica rapidly attacks the basic lining, forming calcium silicate as a slag. The slag from the Gilchrist-Thomas process forms, when ground, a useful phosphatic manure known as *basic slag* (*v.* p. 345).

The melted iron (straight from the blast furnace as a rule) is run into the converter and the blast is turned on. The silicon and manganese react with the iron oxide formed, and while this is happening no flame issues from the mouth of the converter.

$$Si + 3FeO = FeSiO_3 + 2Fe$$
$$Mn + FeO = Fe + MnO.$$

Next the carbon reacts,

$$FeO + Fe_3C = 4Fe + CO,$$

and a large flame issues from the mouth of the converter. When

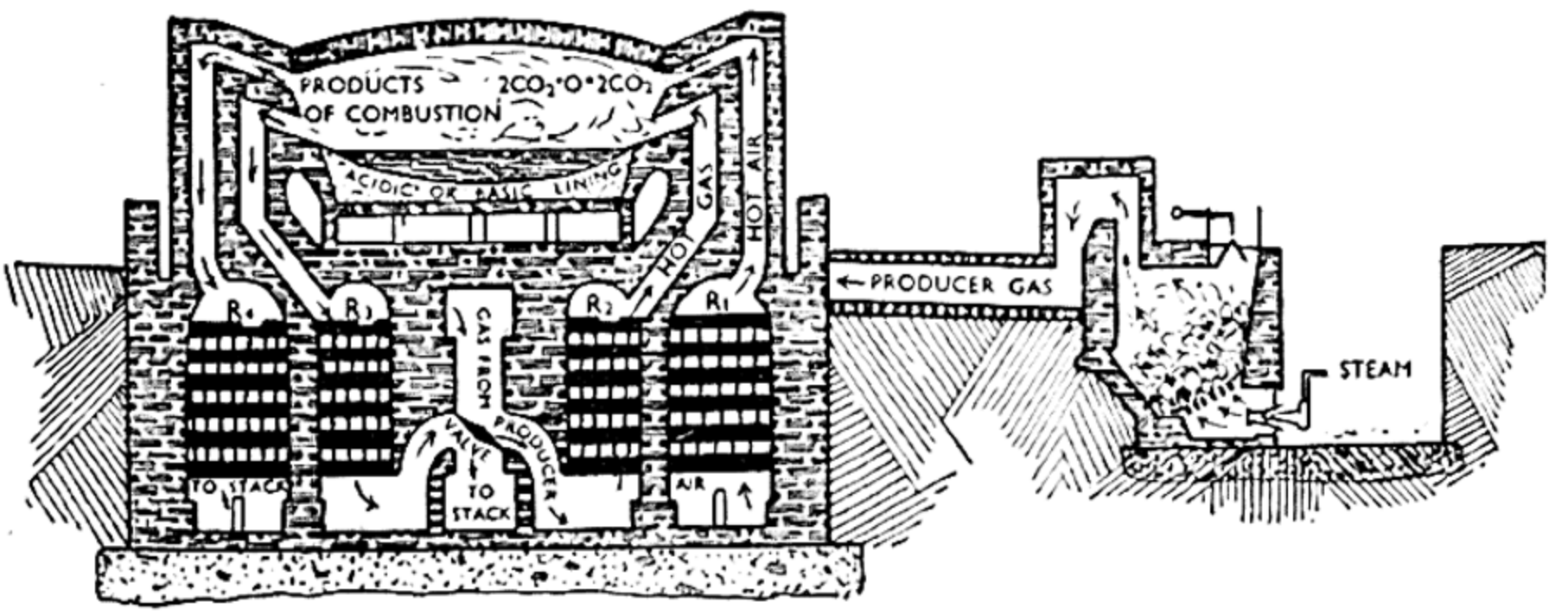



FIG. 190.—Open-hearth process.

the flame dies down the molten metal is nearly pure iron with a certain amount of dissolved oxide. To remove this latter oxide some spiegel-eisen (pig iron containing about 20 per cent. of manganese) is run in. A violent reaction ensues. Most of the manganese is oxidised, thus removing all oxygen from the iron, while the carbon, etc., brings its composition to that of mild steel, say,

Fe, 98·4 per cent. ; C, 0·4 per cent. ; Mn, 0·9 per cent. ; P, 0·1 per cent. ; S, 0·06 per cent. ; Si, 0·1 per cent.

**1143. The open-hearth process** of making steel is by far the most important. In this process pig iron, scrap iron and iron oxide are melted together at a very high temperature. The reactions are similar to those in the puddling furnace (§ 1139), and, as in this process, the iron oxide reacts with the carbon, silicon, manganese and phosphorus of the pig iron, producing the oxides of these elements. Carbon monoxide escapes and burns in the air blast. The other oxides combine with the linings and form slag. The process is simple in principle but in practice it required some new method of heating to raise a huge furnace, containing perhaps 100 tons of iron to a strong white heat (*c.* 1,500° C.).

The furnace illustrated in Fig. 190 is constructed externally of cast iron, and is thickly lined with a resistant firebrick containing much silica. The bed of the furnace is either *basic*, consisting of lime and magnesia, or *acidic*, consisting of refractory sand. The former is used where much phosphorus is present. The furnace is charged with pig iron, scrap steel and some form of iron oxide (hæmatite, etc.). Producer gas from a separate producer is led into the furnace through a 'regenerator,' $R_2$, containing a chequer-work of fire-bricks, which have been previously heated by the products of combustion. Air passes into the furnace through a second hot regenerator, $R_1$. The gas and air burn in the furnace chamber and, since they start at a high temperature, their combustion raises them to very high temperature indeed. The hot products of combustion pass off through another pair of openings and part with their heat to the regenerators, $R_3$, $R_4$, as they leave. When these regenerators are hot and the others cool, the gas and air are switched over to the hot regenerators, $R_3$ and $R_4$, while the hot products of combustion pass away through $R_1$ and $R_2$, heating them once more.

The process has gained its supremacy owing to the ease of controlling the composition of the steel produced, the uniformity of the product and the fact that steel scrap, of which great quantities are available, may be used. It uses fuel, which is a disadvantage as compared to the Bessemer processes, but this is counterbalanced by the better yield of steel.

**1144. Electric Steel.**—Electric furnaces give a peculiarly pure steel very free from sulphur. The furnaces are commonly used for further refining ordinary steel, for the cost of making steel electrically from pig iron and oxide is somewhat high. Steel is melted on a basic lining and some lime with a little sand and fluorspar (to act as a flux) is added. The furnace is closed so as to be free from oxygen, and left for some time. The lime forms calcium carbide and sulphide, while the reducing conditions remove all oxygen. If an alloy-steel (cf. § 1140) is

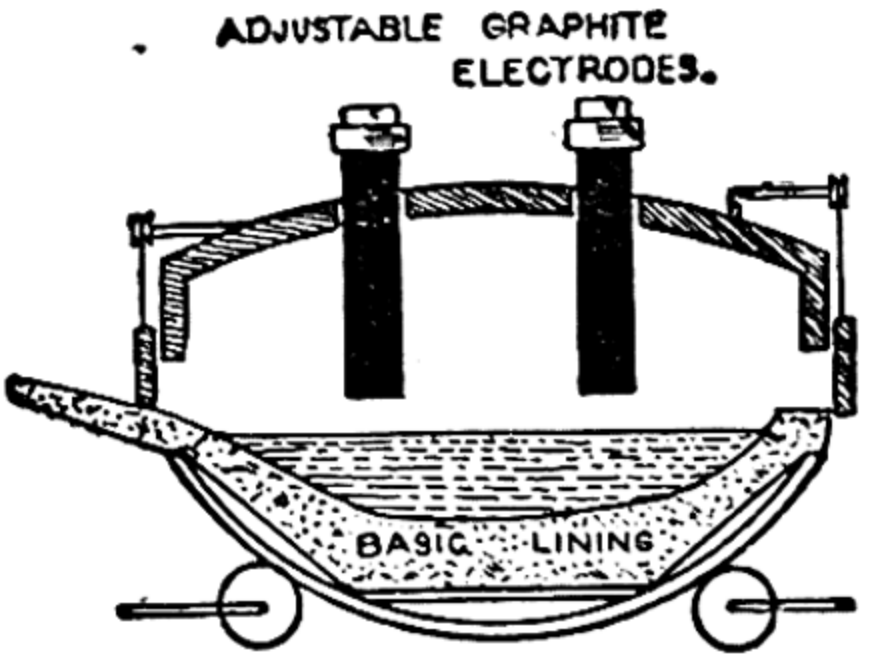



FIG. 191.—Electric steel furnace.

to be made some ferro-manganese, ferro-chromium, etc., are added. The product is of the quality of the fine crucible steel made by cementation, and is much less expensive. The absence of contact with furnace gases renders the castings made from it quite free from gas bubbles, a very important feature in steel which may be required to undergo great stress.

**1145. The Nature of Steel.**—Steel is the most valuable form of iron, combining as it does great strength and hardness with toughness and the possibility of being worked with the hammer. It has, moreover, the valuable property of being hardened or softened, by suitable heat treatment, or tempering.

When steel is cooled slowly—preferably annealed—it is comparatively soft and can be bent, punched, etc., without breaking. If, on the other hand, it is suddenly cooled from a high temperature (750° C. or over) it becomes intensely hard and very brittle, too brittle for most purposes. If the steel is then carefully reheated, it becomes less brittle and less hard, and by regulating the temperature steels suitable for various purposes are obtainable. Thus, steel for razors is reheated very little, for it must be very hard and need undergo no shocks. Steel for chisels, etc., must be heated to a good deal higher temperature, for these, while they should be as hard as possible, must not be at all brittle.

To understand these properties of steel it is necessary to realise that we are not considering a pure material but a mixture of iron and carbon. These elements form a *compound*, *cementite*, $Fe_3C$, and several *solid solutions* of carbon in iron, *e.g.*, *martensite* and *austenite*. Iron itself exists in several allotropic forms.

Pure iron consists of a mass of crystals of *ferrite* or $\alpha$-iron. Iron with a small proportion of carbon (low carbon steel) separates on slow cooling into crystals of pure iron (*ferrite*) and a material of finely laminated structure, called *pearlite* (Plate XVI.), consisting of alternate layers of iron and iron carbide (*cementite*). A steel with more carbon separates into iron carbide (*cementite*) and the same *pearlite* (Plate XVII.). If it is quenched, *i.e.*, suddenly cooled from a high temperature, the separation into iron and iron carbide does not occur, and a very hard and brittle solid solution of carbon in iron remains. These solid solutions (*austenite* or *martensite*) (Plate XVIII.) when gently heated are partly converted into cementite, and this intimate mixture of *cementite* and *martensite* (known as *troostite*) is the main constituent of tempered steel.

Cast iron differs from any type of steel in that it contains particles of free graphite interspersed amongst pearlite and cementite. The other impurities present greatly modify the character of its structure. Its microstructure is not unlike that of Plate XVII., but is interspersed with black particles of graphite.

Very pure iron for laboratory purposes may be prepared by reduction of pure ferric oxide in a current of hydrogen,

$$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O.$$

The electrolysis of a solution of a ferrous salt also yields iron of very high purity.

**1145a. Alloy Steels.**—The addition of other metals, usually in small proportion, to steel gives a number of industrially useful alloys. The composition and properties of these are summed up in the following table.

| ELEMENT | INFLUENCE UPON THE STEEL | USES |
|---|---|---|
| (1) Al | Hardens the metal considerably. Deoxidises, removes Fe oxides. | Used in heat-resisting steels. |
| (2) Cr | Hardens slightly. Increases corrosion and oxidation resistance. Gives some strength at high temperatures. Resists abrasion and wear. | Under 1·5 per cent. in structural steel 0·5–4 per cent. in tool steels. 12–30 per cent. in stainless steels. |
| (3) Co | Gives hardness which persists at red heat. Helps to retain permanent magnetism. | 5–12 per cent. in high speed cutting tools. 15–40 per cent. in cobalt-steel magnets. |
| (4) Cu | Strengthens, and gives resistance to atmospheric corrosion. | *c.* 1 per cent. used to increase strength: *c.* 0·2 per cent. to reduce corrosion. |
| (5) Mn | Hardens markedly and reduces plasticity. Counteracts the brittleness caused by sulphur. | Up to 2 per cent. in most structural steels. |
| (6) Mo | Raises the strength and hardness of steel when hot. Enhances corrosion resistance. | 0·2 per cent. in constructional steels. Up to 9 per cent. in high-speed tools tests. |
| (7) Ni | Strengthens and toughens steel. | Machine-parts and stainless steels. |
| (8) Si | Enhances hardening properties. Deoxidises, and improves corrosion resistance. | Up to 2 per cent. in spring steels. |
| (9) Ti | Hardens, and prevents local depletion of Cr in stainless steels during heat treatment. | Up to 1 per cent. in Cr stainless steels. |
| (10) W | Forms hard, abrasion-resisting, particles in tool steels. Increases strength and hardness at elevated temperatures. | 1–2 per cent. in high-speed tools. 5–9 per cent. in magnet steels. |
| (11) V | Hardens, and favours the retention of permanent magnetism. | Up to 5 per cent. in tool steels. 10 per cent. in magnet steels. |

Steel is usually alloyed with several metals, each enhancing some property, or set of properties. The composition of a typical tool-steel, for instance, is as follows: 5 per cent. Co, 4 per cent. Cr, 14 per cent. W, 0·75 per cent. C, 2 per cent. V, 0·5 per cent. Mo, balance, Fe. The magnet steel, *Vicalloy*, which retains permanent magnetism better than any other known material contains 36–62 per cent. Co, 6–16 per cent. V, and 30–52 per cent. Fe.

**1146. Physical Properties of Pure Iron.**—Iron is a white metal. It melts at the high temperature of *c.* 1,525° C., and it boils in the electric furnace. The melting point is considerably lowered by the presence of carbon. Its density is 7·85, and its specific heat is 0·110. The magnetism of iron is a remarkable phenomenon. Some degree of magnetism is exhibited by almost all elements, some being slightly repelled, others attracted by the magnet. Iron, however, shows a far more powerful degree of magnetism than any other element. The property is only exhibited below 769° C., and is therefore probably connected with the form of iron known as α-iron. Two other forms of iron probably exist at higher temperatures.

**1147. Chemical Properties.**—Iron combines readily with oxygen, burning in air if finely divided and burning vigorously in oxygen, emitting peculiar branched sparks. The magnetic oxide of iron, $Fe_3O_4$, is produced. The ready combustion of iron in a stream of oxygen has been used for cutting large masses of metal, such as armour-plate. The metal is heated locally to a white heat by an oxyacetylene blowpipe and the acetylene is then cut off. By suitable regulation of the oxygen stream the iron is made to burn away in any direction desired.

Iron burns in chlorine, yielding ferric chloride (§ 1170), and in sulphur vapour yielding ferrous sulphide,

$$2Fe + 3Cl_2 = 2FeCl_3$$

$$Fe + S = FeS.$$

It combines directly with the other halogens. Iron forms compounds with phosphorus, carbon and silicon when heated with them, and these are present in cast iron and steel.

Red-hot iron reacts directly with water in the form of steam, the magnetic oxide and hydrogen being formed,

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

**1148. Rusting of Iron.**—With cold water a different type of reaction takes place. Everyone is familiar with the fact that iron, if allowed to become damp, becomes covered with a reddish-yellow material known as rust. Analysis shows this to be a mixture of ferric hydroxide and ferric oxide, varying in composition between the limits $Fe(OH)_3$ or $(Fe_2O_3.3H_2O)$ and $Fe_2O_3$.

The actual process of rusting is, of course, of the highest importance, for the final fate of most iron articles is to be destroyed by rust.

Water alone will not cause rusting to take place, as the following experiment will show. Of two flasks one is filled with tap water and the other with the same water boiled vigorously for twenty minutes to remove all air, and a bright iron or steel nail is placed in each. The surface of the boiled water is covered with an inch of melted vaseline or heavy oil to exclude all air, and the other flask is plugged with cotton wool to admit air but exclude dust. In a year's time the nail in the open flask will be almost wholly converted into rust, while that in the boiled water remains bright. That liquid water and not merely water vapour is needed for rusting is shown by the fact that iron articles kept warm, *e.g.*, a pocket knife kept in a trouser pocket, do not rust despite the fact that water vapour always surrounds them.

There is still some dispute as to whether pure iron will rust in presence of pure water and pure oxygen alone. It seems, however, well established that an impurity in the iron is necessary to cause rusting and that the process is greatly accelerated by the presence of carbon dioxide. If one part of the piece of metal is electropositive with respect to another, that piece will tend to dissolve more rapidly,

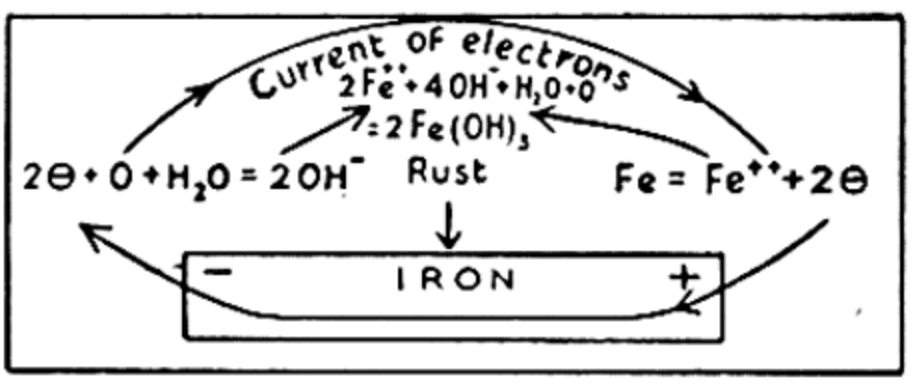



FIG. 192.—Effect of difference in potential in causing rusting of iron.

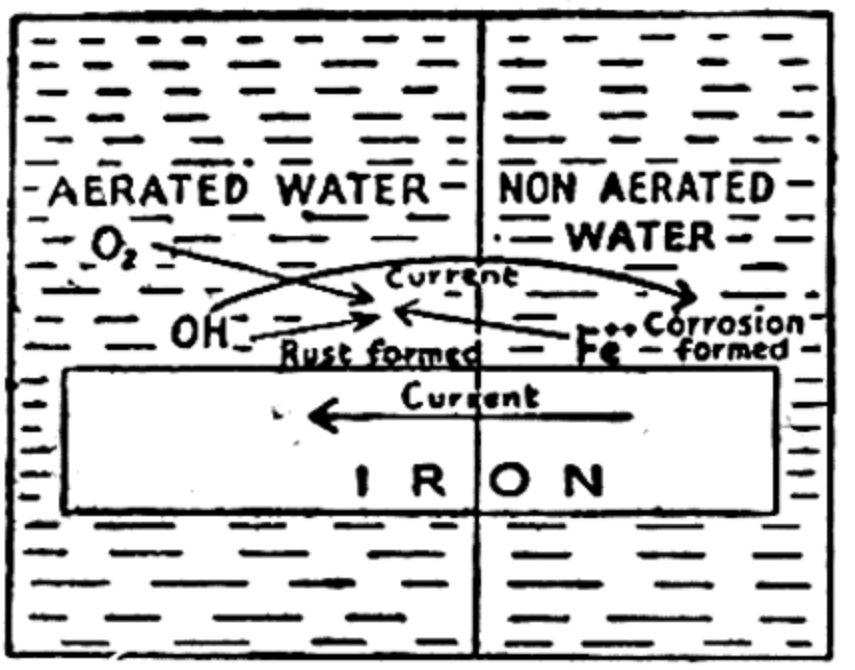



**FIG. 193.—Rusting of iron by differential aëration. Note that in this and Fig. 192, the "current" is figured as flowing from negative to positive, the actual direction of flow of electrons.**

just as pure zinc dissolves in acid more rapidly when in contact with a piece of copper. Ordinary iron and steel contain numerous impurities, which set up centres of rusting, and even if such impurities are not present a scratch on the surface of the iron will start rusting, for the metal which has been strained or deformed by pressure, etc., is electropositive to the unstrained metal.

If, of two adjacent portions of iron, one is more electronegative

(cathodic) and the other more electropositive (anodic), the iron at the latter loses electrons and goes into solution as ferrous ion $Fe^{++}$.

The electrons flow to the cathode where they form $OH^-$. No corrosion occurs at the cathode. The ferrous ion and hydroxyl ion diffuse into the water and where they meet react with the oxygen in the air, giving the very insoluble $Fe(OH)_3$ which deposits. This may occur on the metal or elsewhere. It is noticeable in the experiment described above that rust deposits on the walls of the flask as well as on the metal, showing the latter was at some time dissolved.

It has recently been shown by U. R. Evans that an important cause of rusting is *differential aëration*. If a cell be set up of which one element is iron in water containing dissolved oxygen and the other iron in oxygen-free water, a current flows, the aërated metal being the cathode and the non-aërated the anode. Thus corrosion takes place at the non-aërated portion.

The ferrous ion so produced will dissolve and, where it meets the oxygen of the air, will form ferric hydroxide. Thus corrosion is worst at the deepest part of a rust-spot—the part most remote from the air—and thus a spot of rust tends to "pit" and form a hole.

**1149. Action of Acids upon Iron.**—When acids which are not oxidising agents attack iron, a ferrous salt and hydrogen are formed,

$$Fe + 2HCl = FeCl_2 + H_2.$$

Cast iron and steel evolve their combined impurities (§ 1138) as gaseous hydrides. Thus the hydrogen obtained by dissolving cast iron in acids contains various hydrocarbon gases, such as acetylene, and smaller quantities of hydrogen sulphide, phosphine, arsine, and silicon hydride. The gas is therefore poisonous and malodorous.

Acids which are oxidising agents are reduced. Thus concentrated sulphuric acid yields sulphur dioxide, and both ferrous and ferric sulphates,

$$Fe + 2H_2SO_4 = FeSO_4 + SO_2 + 2H_2O$$
$$2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O + SO_2.$$

A good deal of sulphur is also produced.

Dilute nitric acid is reduced to ammonia, while more concentrated acids give nitrous oxide, nitric oxide and nitrogen peroxide. Ferrous nitrate is formed with very dilute acids, but with more concentrated acids the ferric salt is produced. (For equations, *v.* § 744).

Concentrated nitric acid renders iron *passive*. Iron immersed in concentrated nitric acid or chromic acid remains bright and unaffected, and if removed, appears chemically inert, failing, for

example, to precipitate copper from copper sulphate. It is generally held that this passivity is due to the nitric or chromic acid producing a transparent impervious layer of oxide (probably the magnetic oxide of iron, $Fe_3O_4$), which protects the metal from chemical action.

Iron is not appreciably attacked by alkalis except at high temperatures. If fused with alkalis and an oxidising agent *ferrates* may be formed (p. 766).

**1150. Atomic Weight of Iron.**—That the atomic weight of iron is nearly 56 is shown by the application of Dulong and Petit's law, and also by the vapour densities of its volatile compounds (*e.g.*, the carbonyls).

The equivalents of iron in ferrous and ferric compounds respectively are nearly 28 and 18·7.

Accurate values have been obtained by converting known weights of ferrous chloride and bromide into silver chloride or bromide, and also by the reduction of ferric oxide to the metal. The results obtained indicate a value of 55·84. Iron consists of two isotopes of atomic weight, 56 and 54.

**1151. Iron Hydrides.**—Two iron hydrides, a black powder $FeH_2$, and a black viscous oil $FeH_6$, have been prepared by the action of magnesium phenyl bromide on chlorides of iron.

## Oxides and Hydroxides of Iron.

There are three oxides of iron :—

| | |
|---|---|
| Ferrous oxide . . . . . | $FeO$ |
| Ferrosoferric oxide . . . . | $Fe_3O_4$ |
| Ferric oxide . . . . . | $Fe_2O_3$ |

**1152. Ferrous Oxide FeO.**—This oxide is difficult to prepare in the pure state. It is prepared by reducing ferric oxide heated to 300° C. in a current of hydrogen,

$$Fe_2O_3 + H_2 = 2FeO + H_2O$$

or by heating ferrous oxalate,

$$FeC_2O_4 = FeO + CO + CO_2.$$

The oxide is in both cases likely to contain metallic iron.

Ferrous oxide is a black powder, which burns, often spontaneously, in air, forming ferric oxide.

It is a basic oxide, readily dissolving in acids to form ferrous salts.

The oxide is rarely met with, owing to the difficulty of preserving it from further oxidation.

**1153. Ferrous hydroxide $Fe(OH)_2$** is prepared by the action of solutions of alkalis upon solutions of ferrous salts. If great precau-

tions are taken to exclude air it forms a white precipitate, but if air is present it becomes green and finally brown, ferric hydroxide being formed,

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3.$$

It is difficult to prepare in the dry state for this reason.

Ferrous hydroxide, like other ferrous compounds (*v.* § 1156), is a strong reducing agent.

**1154. Ferrosoferric Oxide, Magnetic Oxide of Iron, $Fe_3O_4$.**—This oxide is formed when iron burns in oxygen or when it is heated in steam. It occurs in nature as *magnetite*. This mineral, which forms shining black crystals or masses, is the lodestone or natural magnet. Naturally occuring pieces of this substance have acquired, as a result of the influence of the earth's magnetism, north and south magnetic poles. Pieces of the natural mineral are true magnets and, if suspended, will point north and south as does a compass needle.

The magnetic oxide is unaffected by heating in air to temperatures easily attainable in the laboratory. At very high temperatures, 1,300° C. and above, it forms ferric oxide. Hydrogen reduces it to the metal.

Acids do not readily attack the oxide, but hydrochloric acid forms ferric and ferrous chloride,

$$Fe_3O_4 + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O.$$

Nitric acid does not affect the oxide, as usually prepared.

**1155. Ferric Oxide $Fe_2O_3$.**—This oxide occurs in vast quantities as a *hæmatite* and *specular iron ore*, which latter is a crystalline form. It is a by-product of the roasting of iron pyrites in the manufacture of sulphur,

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

In the laboratory it may be made by heating ferric hydroxide, or better, by heating ferrous sulphate,

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

The finely divided oxide produced by the latter process is sometimes known as *jeweller's rouge*.

Ferric oxide is a red powder of which the tint varies somewhat with the mode of preparation. The pigments, red ochre, Venetian red, Indian red, are all forms of this oxide. It is an extremely stable substance, unaffected by heat or the action of air or water. Hydrogen and carbon monoxide reduce it to ferrous oxide and then to the metal.

The oxide prepared at a low temperature is fairly easily attacked by acids, but when heated to about 650° C. it glows and is thereafter

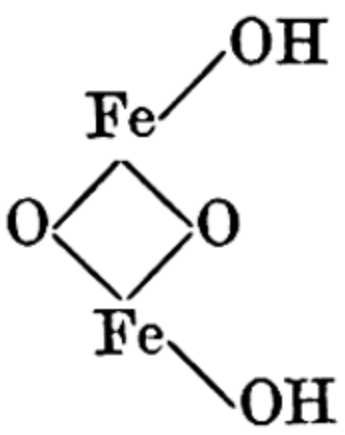
resistant to the action of acids. In this state nitric acid will not affect it, while hydrochloric and sulphuric acids attack it but slowly, forming ferric salts,

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O.$$

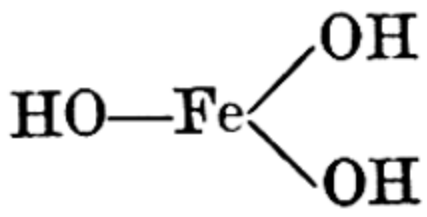
Ferric oxide finds extensive uses as an ore of iron, as a red pigment, as a polishing powder, and as a catalyst in the contact process for the manufacture of sulphuric acid.

*Ferric Hydroxides.* There appear to be more than one ferric hydroxide. It seems that the following hydrates certainly exist :—

$Fe_2O_3 . H_2O$



$Fe_2O_3 . 3H_2O$



The first of these is known as *goethite*, and is the chief constituent of iron rust. The second is the precipitated ferric hydroxide obtained by the action of alkalis on ferric salts.

Ferric hydroxide $Fe(OH)_3$ forms a brown voluminous precipitate. When dried and heated it forms ferric oxide. It is readily soluble in acids, forming ferric salts.

Ferric hydroxide is easily obtained as a colloidal solution. The simplest method of preparing such a solution is to add to 500 c.c. of vigorously boiling water 2 to 3 c.c. of 30 per cent. ferric chloride solution. The colloidal solution may be dialysed (§ 598) to purify it.

*Ferrous acid* $HFeO_2$ or $FeO(OH)$ is obtained by the action of water on sodium ferrite.

*The Ferrites* are compounds of bases with ferric oxide. They are prepared by heating intimate mixtures of the oxides of metals with ferric oxide. In this respect ferric oxide behaves as an acidic oxide.

*Ferrates and perferrates* are also known. The latter form reddish-purple solutions resembling the permanganates, both in colour and in oxidising properties. Potassium perferrate $K_2FeO_4$ may be made by the action of chlorine on a suspension of ferric hydroxide in caustic potash solution,

$$2Fe(OH)_3 + 10KOH + 3Cl_2 = 2K_2FeO_4 + 6KCl + 8H_2O,$$

or by fusing iron filings with potassium nitrate.

## Salts of Iron.

Iron forms two series of salts :—

Ferrous salts, in which iron is divalent.

Ferric salts, in which iron is trivalent.

**1156. General Properties of Ferrous Salts.**—The ferrous salts are, in general, white when anhydrous and pale green when hydrated or in solution. They have a peculiar ' chalybeate ' bitter taste, and are not poisonous in reasonable doses. Ferrous salts are particularly characterised by their *reducing power*.

Ferrous salts are in presence of acids oxidised to ferric salts by the majority of oxidising agents.

The characteristic reaction for the reducing action of a ferrous salt in solution is

$$2Fe^{++} + 2H^{+} + XO = 2Fe^{+++} + H_2O + X$$

If acids are not present basic salts are produced. Among the oxidising agents which will oxidise ferrous salts to ferric salts are free oxygen, nitric acid, the halogens, the permanganates and dichromates.

The oxidation of solutions of ferrous salts by free oxygen is apparently brought about mainly through the hydroxide. Solutions of the salts in water alone contain free ferrous hydroxide as a result of hydrolysis and oxidise rapidly. Strongly acid solutions contain little or no hydroxide and are oxidised only slowly by free oxygen,

$$FeSO_4 + 2H_2O \rightleftharpoons Fe(OH)_2 + H_2SO_4$$

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3$$

$$2Fe(OH)_3 + 2H_2SO_4 = Fe_2(SO_4)_2(OH)_2 + 4H_2O.$$

Brown basic ferric salts are the final product.

Ferrous salts are occasionally used as reducing agents. Thus gold and silver salts are reduced to the metal by solutions of ferrous salts,

$$AuCl_3 + 3FeSO_4 = Au + FeCl_3 + Fe_2(SO_4)_3.$$

Mercuric chloride is reduced to mercurous chloride by ferrous chloride under the influence of light,

$$2Hg^{++} + 2Fe^{++} = 2Fe^{+++} + Hg_2^{++}.$$

Ferrous salts form dark-coloured additive compounds with nitric oxide, such as $FeSO_4.NO$, $FeCl_2.NO$, etc. The colour is probably due to a coloured ion, $[FeNO]^{++}$. Ferrous salts are catalysts for many oxidation and reduction reactions, particularly where the oxidising agent is hydrogen peroxide.

Ferrous salts give, with alkalis, a whitish or greenish precipitate of ferrous hydroxide,

$$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2.$$

With hydrogen sulphide they give a black precipitate of ferrous sulphide,

$$FeSO_4 + H_2S \rightleftharpoons FeS + H_2SO_4,$$

but precipitation does not take place in presence of acids, nor is it complete unless alkalis are present (§ 902). Ferrous salts are distinguished from ferric salts by their reaction with ammonia, which yields a green precipitate with ferrous salts and a brown precipitate with ferric salts. They are also detected even in very small quantity by the blue precipitate of Turnbull's blue given when potassium ferricyanide is added to their solutions (*v.* § 1171).

**1157. Ferrous Carbonate $FeCO_3$** occurs native as spathic iron ore. It is obtained also by adding air-free sodium carbonate solution to air-free ferrous sulphate solution. It forms a white precipitate, which becomes green and then brown in presence of air.

In presence of excess of carbon dioxide the unstable soluble ferrous bicarbonate, $Fe(HCO_3)_2$, is formed (cf. § 1148).

**1158. Ferrous Nitrate** has been prepared as a hydrate, $Fe(NO_3)_2.6H_2O$. It is very unstable and is best prepared by grinding equivalent quantities ferrous sulphate with lead nitrate in the presence of dilute alcohol, in which lead sulphate is very insoluble,

$$FeSO_4.7H_2O + Pb(NO_3)_2 = Fe(NO_3)_2.6H_2O + PbSO_4 \downarrow + H_2O.$$

Evaporation at a low temperature yields green crystals very soluble in water. They readily decompose, forming basic ferric nitrate.

**1159. Ferrous Sulphide FeS.**—Ferrous sulphide is obtained by heating iron with sulphur or by the action of hydrogen sulphide on a ferrous salt.

It is a black insoluble substance. Heated in air it is oxidised to ferrous sulphate and on further heating to ferric oxide,

$$FeS + 2O_2 = FeSO_4,$$
$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

It dissolves in acids, forming ferrous salts and hydrogen sulphide and is the usual source of the latter gas (§ 98).

**1160. Ferrous Sulphate, Green Vitriol, $FeSO_4.7H_2O$.**—Ferrous sulphate is the most important of the ferrous salts. It occurs native as *melanterite* or 'copperas,' which results from the oxidation of pyrites. This substance was known to the Greeks and Romans, who used it both medicinally and in the preparation of ink. The salt is prepared commercially by stacking iron pyrites in heaps and

exposing them to the action of air and water. Ferrous sulphate and sulphuric acid result, the latter being neutralised by scrap-iron,

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$
$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

The liquors are boiled down and crystallised. Ferrous sulphate, so made, usually contains traces of other metals. The pure salt is best made by heating pure iron wire with dilute sulphuric acid (*c.* 30 per cent.) until no more will dissolve. The hydrogen evolved, which has an offensive odour if the iron is not free from impurities, may be led into a Bunsen flame and burned. The solution is heated to boiling and rapidly filtered into a basin containing a few drops of the dilute acid. The salt crystallises and should be well dried on filter papers at a temperature not above 30° C. A product free from ferric sulphate may be made by precipitating the salt with alcohol.

Ferrous sulphate is white when anhydrous, but the usual salt, the heptahydrate, is green.

When heated, water of crystallisation is first lost and the salt then decomposes, forming first ferric sulphate and then ferric oxide, giving off sulphur dioxide and sulphur trioxide,

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

This process was once used to prepare sulphuric acid, whence its name *oil of vitriol.*

Solutions of ferrous sulphate are valuable reducing agents (*v.* § 1156). Ferrous sulphate forms a compound, $FeSO_4.NO$ (which has been isolated as unstable red crystals) with nitric oxide, and the colour of this has been utilised in the ' brown-ring test ' for nitric acid or nitrates (*v.* § 749).

Ferrous sulphate is used in the preparation of nitric oxide (§ 712 (3) ) and of ferric sulphate and ferric oxide. It is also used in the manufacture of ink, which is made from the gallic acid from gall-nuts and ferrous sulphate. Inks of this composition have been used for more than a thousand years, and none of the more recently discovered colouring matters has the same degree of permanence. Modern inks usually contain aniline dyes, which give a strong colour, and some iron gallate which gives permanence.

*Ferrous ammonium sulphate* $FeSO_4.(NH_4)_2SO_4.6H_2O$. This salt is made by adding ammonium sulphate solution saturated at 40° C. to ferrous sulphate dissolved in as little air-free water as possible at the same temperature. The solutions should be faintly acid. On cooling, pale green crystals deposit. It is used in analytical work in preference to ferrous sulphate, since its solutions do not oxidise

so quickly as those of the latter salt. It is readily soluble in water, 100 gms. of which dissolve 20 gms. of the salt at 15° C.

Many other double salts derived from ferrous sulphate are known.

**1161. Ferrous Chloride $FeCl_2$.**—The anhydrous salt is obtained by heating iron filings in a current of hydrogen chloride,

$$Fe + 2HCl = FeCl_2 + H_2,$$

or better by igniting ammonium tetrachloroferrite (described below) in absence of air, and the hydrated salt is obtained by dissolving pure iron in air-free dilute hydrochloric acid with the precautions described under Ferrous Sulphate (§ 1160).

Anhydrous ferrous chloride forms white scales, and the usual hydrated salt, $FeCl_2.4H_2O$, forms greenish-blue monoclinic crystals.

The salt is very soluble in water, 100 gms. of which dissolve about 67 gms. of the anhydrous salt at 15° C.

Anhydrous ferrous chloride, when heated in air, is oxidised to ferric chloride and oxide,

$$12FeCl_2 + 3O_2 = 2Fe_2O_3 + 8FeCl_3.$$

In addition to the usual properties of ferrous salts (§ 1156) and chlorides (§ 1057) it shows a tendency to form complex loose compounds. Thus with ammonia it forms $FeCl_2.6NH_3$ and $FeCl_2.2NH_3$, with nitric oxide it forms the compound $FeCl_2.NO$, which is very unstable and has not been isolated, and with nitrogen peroxide, $4FeCl_2.NO_2$, which is fairly stable. It forms numerous double salts, of which ammonium tetrachloroferrite or ferrous ammonium chloride, $(NH_4)_2FeCl_4$ or $FeCl_2.2NH_4Cl$, is the best known. The salt is prepared by crystallising a mixture of ferrous and ammonium chlorides with due precautions to exclude air.

**1162. Ferrosoferric Chloride $Fe_3Cl_8 . 18H_2O$.**—There exists one salt intermediate between the ferrous and ferric compounds and apparently derived from ferrosoferric oxide $Fe_3O_4$. This salt, ferrosoferric chloride, is obtained by dissolving magnetic oxide of iron in concentrated aqueous hydrochloric acid and evaporating the solution over sulphuric acid. It forms a yellow deliquescent mass.

**1163. General Properties of Ferric Salts.**—The ferric salts, in which iron is tervalent, are for the most part white or yellow. Their solutions are yellow, though the presence of colloidal ferric hydroxide often gives them a deeper colour. Ferric salts are more easily hydrolysed than ferrous salts, for ferric hydroxide is a weaker base than ferrous hydroxide. Thus ferrous carbonate and acetate exist while ferric carbonate and acetate are hydrolysed to the acid and base. In general it is found that the higher salts of a metal are always more readily hydrolysed than the lower salts.

Ferric salts are mild oxidising agents. They are reduced to ferrous salts by nascent hydrogen, sulphur dioxide, iodides, zinc, and other electropositive metals, thiosulphates and stannous chloride. The reactions are discussed under the headings of the reducing agents in question, but equations may here be given to show the course of the reactions,

$$FeCl_3 + H = FeCl_2 + H_2$$
$$2Fe^{+++} + H_2O + SO_3^{--} = 2Fe^{++} + 2H^+ + SO_4^{--}$$
$$Fe^{+++} + I^- \rightleftharpoons Fe^{++} + I$$
$$2Fe^{+++} + Zn = 2Fe^{++} + Zn^{++}$$
$$2Fe^{+++} + 2S_2O_3^{--} = 2Fe^{++} + S_4O_6^{--}$$
$$2Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++}.$$

Ferric salts of certain organic acids or mixtures of ferric salts and organic compounds are reduced under the influence of light. The reduction of ferric oxalate is used in the well-known blue-print process. The sensitive paper used for this purpose has been previously soaked in a solution of ferric oxalate or other organic ferric salt. It is exposed under a negative and where light falls on it ferrous oxalate is formed.

$$Fe_2(C_2O_4)_3 = 2FeC_2O_4 + 2CO_2.$$

The paper is then developed with a solution of potassium ferricyanide solution, which gives *Turnbull's blue* with the ferrous salt formed by the action of light; the unreduced ferric salt is washed out of the print.

**1164. Ferric Nitrate $Fe(NO_3)_3$** is obtained by acting on iron with dilute nitric acid. Ten grams of the metal may be dissolved in 100 gms. of nitric acid (sp. gr. 1·3) and an equal volume of nitric acid (sp. gr. 1·4) added. Crystals of $Fe(NO_3)_3.9H_2O$ separate.

When quite pure it forms colourless crystals. It finds a use as a mordant in dyeing.

**1165. Ferric Carbonate** does not exist, iron in this respect resembling most other trivalent metals.

**1166. Ferric Thiocyanate $Fe(CNS)_3$.**—This salt is of interest on account of its deep red colour. It is formed when a thiocyanate is added to a solution of a ferric salt, a reaction which is used as a test for ferric iron. It crystallises in deep red cubes. Solutions of ferric thiocyanate are decolorised by weak organic acids, and even dilution alone is sufficient to reduce the coloration. These facts are accounted for if we reflect that, since the ferric ion is yellow and the thiocyanate ion is colourless, it must be the undissociated ferric thiocyanate which is blood-red in colour. This dissociates in solution

$$\underset{\text{Red.}}{Fe(CNS)_3} \rightleftharpoons \underset{\text{Yellow.}}{Fe^{+++}} + \underset{\text{Colourless.}}{3(CNS)^-}.$$

Dilution increases the degree of ionisation and so decreases the colour. Acids add hydrion, which combines with and removes the thiocyanate ion, thus causing the ferric thiocyanate to dissociate further.

**1167. Ferric Sulphide $Fe_2S_3$** is obtained by the action of hydrogen sulphide on ferric oxide. This reaction is used in the purification of coal-gas.

**1168. Iron Disulphide, Iron Pyrites, $FeS_2$,** is a very common mineral. It occurs in hard yellow cubes of brassy appearance. Another form of the same substance is *marcasite*, which has the same metallic appearance but a nearly white colour.

Pyrites is supposed to have been formed by the reduction of ferrous sulphate contained in water by organic matter ; but this can hardly account for the vast masses of the mineral found in Spain and other places.

Pyrites, when heated in air, burns, forming ferric oxide and sulphur dioxide, and is the cheapest source of the latter gas. Exposed to the action of air and water it becomes oxidised to ferrous sulphate and sulphuric acid,

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4.$$

**1169. Ferric Sulphate $Fe_2(SO_4)_3$.**—The anhydrous salt may be made by heating the hydrate, which is most readily obtained by heating ferrous sulphate with nitric and sulphuric acids.

Twenty grams of ferrous sulphate are dissolved in 20 c.c. of dilute sulphuric acid (15 per cent.). The liquid is heated to boiling in a 150 c.c. porcelain dish and concentrated nitric acid is added 1 c.c. at a time until a specimen, on dilution, gives no blue colour with freshly-prepared potassium ferricyanide solution. The operation should be performed in the fume cupboard. The solution is evaporated to about half its bulk, when it will solidify on cooling to a whitish mass of ferric sulphate. The anhydrous salt and the usual hydrate, $Fe_2(SO_4)_3.9H_2O$, are white solids. When heated ferric sulphate decomposes, giving ferric oxide and sulphur trioxide,

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

In solution the salt is readily hydrolysed, precipitating rather indefinite brown basic salts,

$$Fe_2(SO_4)_3 + 2H_2O \rightleftharpoons Fe_2(SO_4)_2(OH)_2 + H_2SO_4.$$

These precipitates redissolve in acids.

Ferric sulphate forms *alums* (§ 493) with the sulphates of the alkali metals.

*Potassium iron alum* $K_2SO_4.Fe_2(SO_4)_3.24H_2O$, known as iron alum, is made by mixing concentrated solutions of the sulphates of

the two metals. The alum is often slow to separate out, but ultimately crystallises as pale violet octahedra. It is a useful salt in that it is one of the few ferric compounds which can be well-crystallised and so obtained in a state of purity, which ensures a constant composition. It is therefore used as an analytical standard of ferric iron. It also finds a use as an indicator in the titration of silver (§ 321).

**1170. Ferric Chloride $FeCl_3$.**—The anhydrous salt is prepared in the laboratory by passing a current of dry chlorine over heated iron. A bundle of iron wires (about 1 mm. in diameter) may be placed in a wide tube (*c.* 2 cm.) connected to a bottle as in Fig. 194. Chlorine, which must be well dried with sulphuric acid, is led over the gently heated metal, which burns, yielding the volatile chloride, which condenses in the bottle as glistening crystals.

The anhydrous salt made in this way forms lustrous brown-black scales, which volatilise below 300° C.

The hydrated salt, which is the form of ferric chloride commonly met with in the laboratory, consists mainly of the dodecahydrate, $Fe_2Cl_6.12H_2O$ ; and three other hydrates also exist. The crystallised salt may be prepared by the action of hydrochloric acid on ferric oxide.

Ferric chloride is exceedingly soluble in water, 100 gms. of the latter dissolving 92 gms. of ferric chloride at 20° C., and no less than 536 gms. at 100° C. The solubility curve is very complex as a result of the existence of so many hydrates.

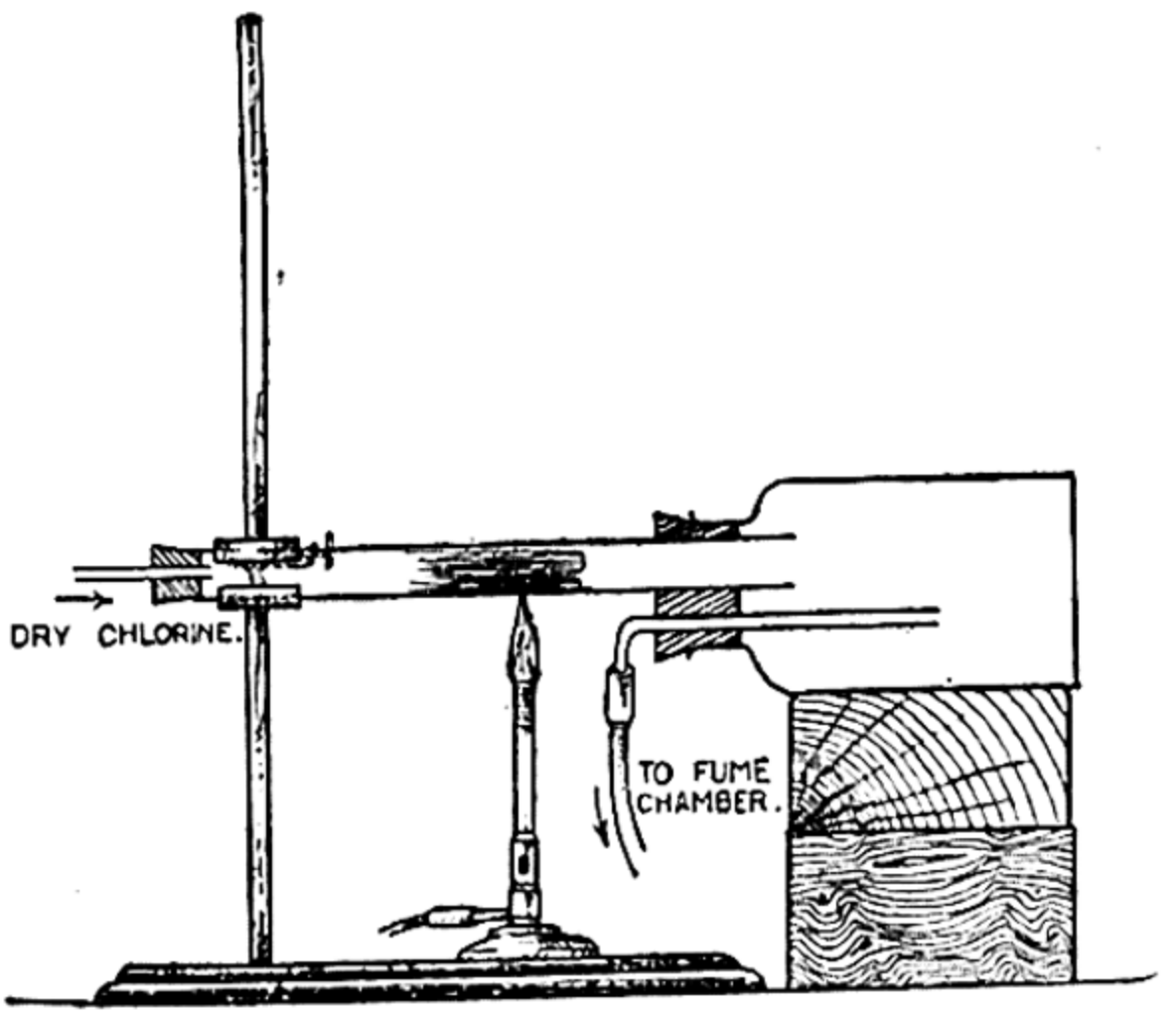



FIG. 194.—Preparation of anhydrous ferric chloride.

Ferric chloride is soluble in ether, and it is possible to remove ferric chloride from a solution by shaking it with this solvent.

Anhydrous ferric chloride decomposes when heated to 500° C., giving ferrous chloride and chlorine. The solid is reduced by hydrogen to ferrous chloride.

Solutions of ferric chloride are brown to yellow in colour. They are rapidly hydrolysed by water and become dark in colour,

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl,$$

from the production of colloidal ferric hydroxide (§ 1155).

Ferric chloride is reduced to ferrous chloride by suitable reagents (§ 1163).

Ferric chloride forms many double salts.

*Ammonium tetrachlorferrate* $NH_4FeCl_4$, or ferric ammonium chloride, is obtained by heating ammonium chloride with anhydrous ferric chloride. It is interesting as having a definite boiling point, 386° C.

**1171. Prussian Blue.**—The *ferrocyanides* and *ferricyanides* are discussed in Chapter XV., but something may be said here about the ferrocyanides and ferricyanides of iron. Numerous blue materials are derived from iron salts and ferro- or ferri-cyanides. It is probable that these are : (*a*) Colloidal in character, (*b*) mixtures.

The formation of these compounds may be summarised as below

| | Ferrous salt. | Ferric salt. |
|---|---|---|
| Ferrocyanide . . | White precipitate | Prussian blue |
| Ferricyanide . . . | Turnbull's blue | Brown solution |

It would be thought from the above that Prussian blue was ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$, and Turnbull's blue ferrous ferricyanide $Fe_3[Fe(CN)_6]_2$, but in actual fact analyses show that they are identical. The reason is that the ferric ion oxidises the ferrocyanide ion giving some ferrous ion and ferricyanide ion. Ferrous ion, also, reduces the ferricyanide ion to some extent to ferrocyanide ion, itself forming ferric ion. Thus a mixture of potassium ferricyanide with a ferrous salt or of potassium ferrocyanide with a ferric salt contains all four ions.

$$Fe^{++},\ Fe^{+++},\ Fe(CN)_6'''',\ Fe(CN)_6'''.$$

$K^+$ ion will also, of course, be present. These ions react, giving a mixture of blue compounds chiefly ferrous potassium ferricyanide, ferric potassium ferrocyanide with some ferrous ferricyanide and ferric ferrocyanide.

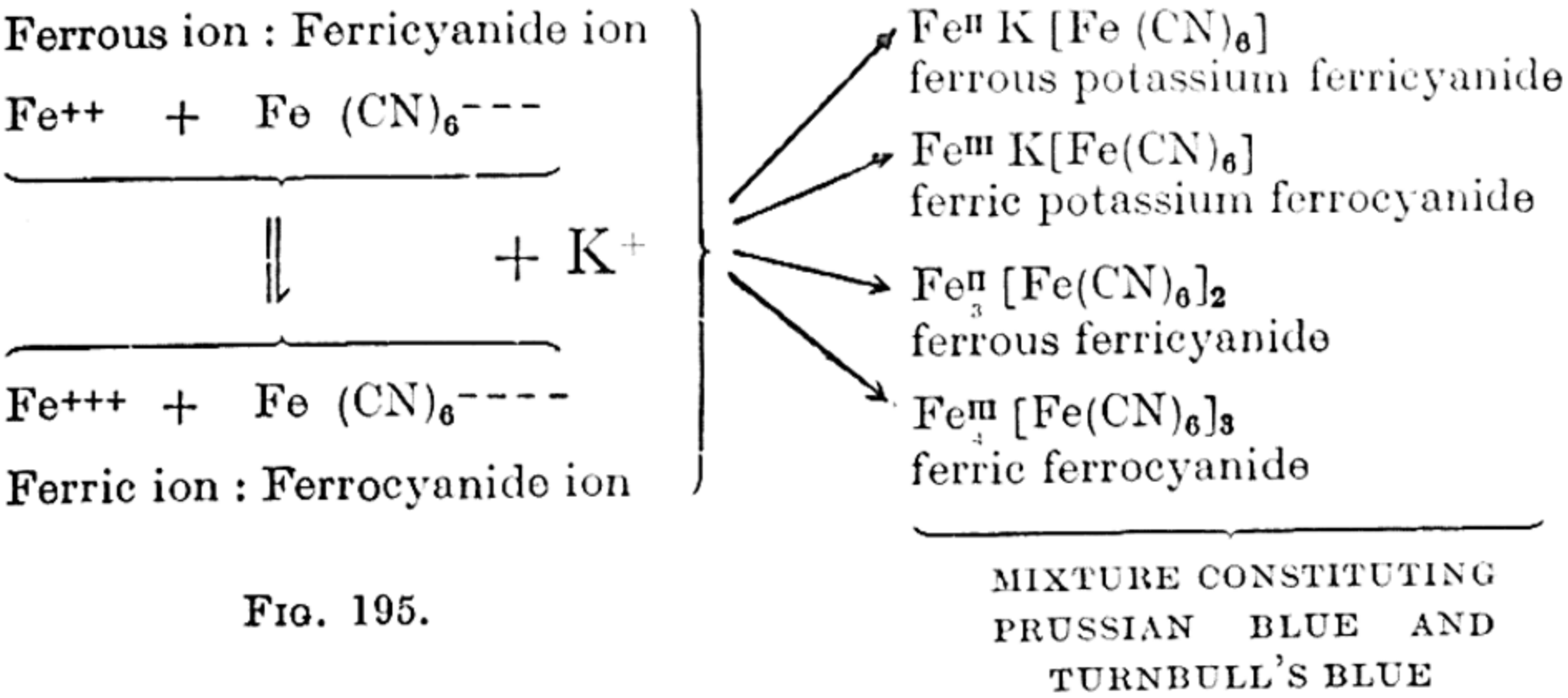



FIG. 195.

The forms known as "soluble" and "insoluble Prussian blue" differ only in the size of their particles.

*Insoluble Prussian blue* is formed when an excess of a ferric salt is mixed with a ferrocyanide as a deep blue precipitate which does not dissolve in water.

*Soluble Prussian blue* is obtained when cold neutral solutions of a ferric salt and a ferrocyanide are mixed. It is readily soluble in excess of water.

*Other Prussian blues* are formed by oxidising ferrous ferrocyanide which is obtained as a white precipitate when a ferrous salt and a ferrocyanide are mixed. These blues resemble soluble Prussian blue but differ from it in that they are insoluble in oxalic acid solution.

*Ferrous ferrocyanide* is formed as a white precipitate when a pure ferrous salt is mixed with a ferrocyanide. It oxidises rapidly in air, forming Prussian blue. This method of preparing Prussian blue is used on the large scale. The oxidation of the white ferrocyanide to blue ferric ferrocyanide is usually accomplished by means of nitric acid.

Prussian blue is a deep blue powder with a coppery lustre. It finds a considerable use as a pigment, as it has great colouring power and is also very permanent. It is a stable substance, being attacked only by concentrated acids and alkalis.

**1172. Iron Carbonyls.**—Iron forms a series of interesting compounds with carbon monoxide. They include :—

| | |
|---|---|
| Iron pentacarbonyl . . . . . | $Fe(CO)_5$ |
| Diferrononacarbonyl . . . . . | $Fe_2(CO)_9$ |
| Triferrododecacarbonyl . . . . | $Fe_3(CO)_{12}$ |

Iron pentacarbonyl is obtained by the action of carbon monoxide on finely divided iron, obtained by the reduction of ferrous oxalate with hydrogen. The carbonyl is distilled over at 120° C. It forms a thick yellow liquid, soluble in organic solvents. It is decomposed by light.

An interesting case has recently (1930) been reported, where a cylinder of coal gas, overlooked for thirty years, was found to burn with a peculiar luminous and smoky flame. It was found that the gas contained an appreciable amount of iron pentacarbonyl. This shows that iron and carbon monoxide combine to an appreciable extent in the cold. It is not unlikely that many interesting facts remain undiscovered owing to the short time usually allowed for a chemical reaction.

The other iron carbonyls are solids. The nonacarbonyl is obtained by the decomposition of the pentacarbonyl. For the structure of these, see § 1217a.

**1173. Detection and Estimation of Iron.**—All iron compounds when mixed with sodium carbonate and heated on charcoal in the reducing flame, yield metallic iron as a grey-black powder, attracted by a magnetised knife-blade.

Ferrous salts and ferric salts are detected by their characteristic reactions with ferrocyanides, ferricyanides and thiocyanates, which are discussed above and on p. 768.

Iron is estimated gravimetrically by oxidising it to the ferric state with nitric acid and precipitating it as ferric hydroxide by means of ammonia, or if aluminium is present by means of an excess of caustic soda (§ 486). The ferric hydroxide is filtered off, washed, ignited and weighed.

Iron is determined volumetrically by first reducing it to the ferrous state and then titrating it with potassium permanganate (*v.* § 1120). The reduction may be conducted by means of nascent hydrogen, sulphur dioxide, or stannous chloride. For details a text-book of chemical analysis should be consulted.

Ferric iron can be also determined by reduction with titanous chloride (§ 659).

## COBALT Co, 58·94

**1174. Historical.**—The metal cobalt has only been known since 1733. Its minerals have, however, been used for colouring pottery since the later Egyptian period. The name is said to be the same as the German *Kobold*, a gnome or earth-dwelling spirit. This name was given to a certain ore, apparently because it was poisonous. In 1540 it was discovered that this ore would colour glass, and in 1733 Brandt extracted a metal from it.

**1175. Occurrence.**—Cobalt is found chiefly as arsenides. *Cobalt glance* CoAsS, *smaltite* $CoAs_2$ are common minerals. Near Ontario, in Canada, there are considerable deposits of these minerals associated with nickel and silver and these are the most important source of the metal.

**1176. Extraction.**—The ore is crushed, ground and smelted in small blast furnaces. Arsenic trioxide is volatilised, and is condensed and sold (p. 579); the earthy matter forms a slag, which is rejected. The remainder of the ore is separated into two layers, one a *speiss* of cobalt, nickel, iron and copper arsenides, the other crude silver.

The "speiss" is crushed and roasted with common salt, which converts it into cobalt, nickel and copper chlorides. The copper is

removed by precipitation on scrap iron (cf. § 277), and the cobalt and nickel are precipitated as hydroxides by caustic soda. The precipitate is dried, giving a mixture of the oxides of cobalt and nickel.

Several methods of separating cobalt and nickel are in use. Beside the Mond process (§ 1201) we may mention the following.

The mixed oxides of cobalt and nickel are dissolved in hydrochloric acid and neutralised with chalk. A solution of bleaching powder is then added. The cobalt is precipitated as the hydrated oxide, almost free from nickel,

$$2CoCl_2 + 2Ca(OH)_2 + CaOCl_2 + H_2O = 2Co(OH)_3\downarrow + 3CaCl_2.$$

This hydroxide is dried and heated, when it forms cobalto-cobaltic oxide,

$$12Co(OH)_3 = 4Co_3O_4 + 18H_2O + O_2.$$

The oxide so obtained may be reduced to metal by reduction with carbon, hydrogen, carbon monoxide or aluminium. The latter is perhaps the simplest method of obtaining the compact metal. Cobalt may also be prepared by electrolysing cobalt ammonium sulphate.

**1177. Properties.**—Cobalt is a white metal, rather harder than pure iron or nickel. It is slightly magnetic. Cobalt melts at 1,490° C. Its density is 8·8. It absorbs up to a hundred times its volume of hydrogen (cf. nickel and palladium, §§ 1202, 1222).

Cobalt is not oxidised by the air, dry or moist, at ordinary temperatures. At a red heat it is slowly oxidised. It is attacked by the halogens.

It is slowly attacked by acids, dilute hydrochloric and sulphuric acids giving cobalt salts and hydrogen. Nitric acid also attacks it.

The largest single use of cobalt is in high-speed cutting-tools, which retain their hardness even at a red heat. Those first developed contained 12 per cent. Co, 4 per cent. Cr, 20 per cent. W, 2 per cent. V, 62 per cent. Fe ; more recently tools made of the extremely hard tungsten carbide supported in a matrix of cobalt (12 per cent. Co, 82 per cent. W, 5 per cent. C), have been used. Vicalloy, 50 per cent. Co, 40 per cent. Fe, 10 per cent. V, retains permanent magnetism more tenaciously than any other known material.

**1178. Atomic Weight of Cobalt.**—From Dulong and Petit's law and from its position in the Periodic table a figure of about 59 would be expected.

According to this value cobalt is bivalent in most of its compounds, the equivalent being about 30. The most accurate method of determining the atomic weight is the conversion of the chloride and bromide into the corresponding silver compounds. A value of 58·94 has been adopted.

**1179. Cobalt Oxides and Hydroxides.**—Cobalt forms three well-defined oxides and a very unstable peroxide,

| | |
|---|---|
| Cobaltous oxide . . . . | $CoO$ |
| Cobalto-cobaltic oxide . . . | $Co_3O_4$ |
| Cobaltic oxide . . . . . | $Co_2O_3$ |
| Cobalt peroxide . . . . | $CoO_2$ |

The first three of these are basic in character. The last is acidic.

**1180. Cobaltous Oxide CoO.**—This oxide is best prepared by careful reduction of cobaltic oxide in a current of hydrogen. It forms a grey powder. When heated in air it forms cobalto-cobaltic oxide $Co_3O_4$. When heated in a current of hydrogen the metal is formed. It is basic in character and yields cobaltous salts when treated with acids.

**1181. Cobaltous Hydroxide $Co(OH)_2$,** obtained by the action of alkalis on cobaltous salts, exists in two modifications, one blue and the other rose-pink. Like ferrous hydroxide and manganous hydroxide it absorbs oxygen from the air, forming brown cobaltic hydroxide.

**1182. Cobalto-cobaltic Oxide $Co_3O_4$** is the oxide of cobalt usually met with. It is obtained by strongly heating cobalt nitrate,

$$3Co(NO_3)_2 = Co_3O_4 + 6NO_2 + O_2.$$

Cobalto-cobaltic oxide is a black powder. It is reduced by hydrogen to the metal.

It gives cobaltous chloride and chlorine when dissolved in hydrochloric acid,

$$Co_3O_4 + 8HCl = 3CoCl_2 + Cl_2 + 4H_2O.$$

**1183. Cobaltic Oxide $Co_2O_3$** is said to be obtained as a black powder when cobalt nitrate is gently heated. It has, however, been stated that the product is cobalto-cobaltic oxide with some adsorbed oxygen.

**1184. Cobaltic Hydroxide $Co(OH)_3$** is obtained by the action of alkaline oxidising agents, such as sodium hypochlorite on a cobalt salt.

With acids at low temperatures brown solutions, probably containing cobaltic salts, are obtained. On warming these decompose. With hydrochloric acid chlorine is obtained,

$$2Co(OH)_3 + 6HCl = 2CoCl_2 + 6H_2O + Cl_2.$$

**1185. Cobalt Peroxide** is obtained by the action of certain oxidising agents on cobaltous salts. Stable salts, known as *cobaltites*, *e.g.*, $BaCoO_3$, have been prepared.

**1186. General Properties of Cobaltous Salts.**—Cobaltous salts are

either pink or blue. The pink colour is seen only in the hydrated salts. In solution they have a strong pink colour due to the cobaltous ion $Co^{++}$.

Cobaltous salts give pink or blue precipitates of the hydroxide with caustic potash or soda. The precipitate formed by ammonia redissolves, in excess of that reagent, and on oxidation forms various cobaltammine salts (§§ 1235 *seq.*).

With hydrogen sulphide in neutral or alkaline solution black cobalt sulphide CoS is precipitated.

Sodium carbonate gives a reddish precipitate of basic cobalt carbonate.

Hypochlorites precipitate black cobaltic hydroxide.

**1187. Cobaltous Carbonate $CoCO_3$** is a bright red powder. As obtained by precipitation of a cobalt salt with sodium carbonate it is a basic salt, $CoCO_3.nCo(OH)_2$.

**1188. Cobalt Carbonyls.**—Cobalt forms carbonyls (§ 1172a). Two of these are known, $Co_2(CO)_8$ and $Co_4(CO)_{12}$. The former is made by the action of carbon monoxide at 40 atmospheres pressure and 150° C. on finely divided cobalt. It forms orange crystals. On heating to 60° C. $Co(CO)_3$ is formed in black crystals.

**1189. Cobaltocyanides and Cobalticyanides.**—These are stable salts and resemble in formula and general behaviour the ferrocyanides and ferricyanides. The cobaltocyanides are, however, much more readily oxidised than the ferrocyanides.

**1190. Cobalt Silicate, Smalt,** is the most important compound of the element. It is made by fusing cobalt oxide with silica and potassium carbonate. A glass of a very deep blue colour is formed. This is ground and forms a very stable deep blue pigment.

The blue colour of cobalt silicate makes cobalt compounds useful for colouring porcelain and glass. The Chinese blue porcelain and also almost all modern blue china is coloured with cobalt compounds in a greater or less state of purity. Copper gives a greenish blue colour, cobalt a reddish blue.

*Thénard's blue* is probably an aluminate of cobalt. It is obtained by mixing a cobalt compound (phosphate preferably) with freshly-precipitated alumina. The mass is heated to redness and finally ground with water. It forms a fine blue pigment of great permanency. Its formation is used as a test for cobalt.

*Rinman's green* is made like Thénard's blue, substituting zinc oxide for alumina. It is probably a cobalt zincate.

**1191. Cobaltous Nitrite $Co(NO_2)_2$** has not been isolated but the *cobaltinitrites* (derived from cobalt*ic* nitrite) are an important series of salts.

**1192. Potassium Cobaltinitrite $K_3Co(NO_2)_6nH_2O$.**—This salt is obtained when potassium nitrite is added to a solution of a cobalt salt acidified with acetic acid.

$$2Co^{++} + 2H^{+} + 2HNO_2 = 2Co^{+++} + 2H_2O + 2NO$$

$$Co^{+++} + 6NO_2^- = [Co(NO_2)_6]^{---}$$
$$3K^+ + [Co(NO_2)_6]^{---} = K_3[Co(NO_2)_6].$$

forms a bright yellow insoluble crystalline precipitate. Nickel forms a soluble nickelinitrite and so the precipitation of the cobaltinitrite gives at once a test for cobalt and a means of separating it from nickel. It is also used as a means of testing for potassium and ammonium (§ 267).

The salt is used as a pigment and also for colouring porcelain blue.

Other cobaltinitrites are known. The structure of potassium cobaltinitrite is

$$K_3^{+++}\begin{bmatrix} NO_2 & NO_2 & NO_2 \\ & Co & \\ NO_2 & NO_2 & NO_2 \end{bmatrix}^{---}$$

The potassium and cobaltinitrite ions are combined by electrovalency, the cobalt atom and nitrite groups by co-ordinate valencies (*v.* §§ 1235–8).

Thus the salt does not yield nitrite ions as it would if the formula were $(KNO_2)_3.Co(NO_2)_3$, potassium cobaltic nitrite.

**1193. Cobalt Sulphide CoS** is obtained by the action of ammonium sulphide on a cobalt salt,

$$(NH_4)_2S + CoCl_2 = 2NH_4Cl + CoS.$$

The sulphide is black in colour. When first precipitated it dissolves in acids but after standing, or on heating, it becomes insoluble in hydrochloric acid, probably owing to oxidation.

**1194. Cobalt Sulphate $CoSO_4 . 7H_2O$** is made by the usual methods. It is a red salt, easily soluble in water, 100 gms. of which dissolve 36 gms. of the anhydrous salt at 20° C. and 83 gms. at 100° C.

When strongly heated it first becomes anhydrous and then at a white heat decomposes, leaving cobalto-cobaltic oxide. In other respects it has the ordinary properties of cobalt salts.

*Cobalt ammonium sulphate* $CoSO_4.(NH_4)_2SO_4.6H_2O$ (analogous to ferrous ammonium sulphate) forms pink crystals.

**1195. Cobaltous Chloride $CoCl_2$.**—The anhydrous salt can be obtained by the action of chlorine on metallic cobalt. The salt forms numerous hydrates, the *hexahydrate* $CoCl_2.6H_2O$ being commonly met with. It is best made by dissolving cobalt oxide in hydrochloric acid and evaporating till crystallisation occurs.

Cobalt chloride is blue when anhydrous and pink when hydrated. The salt is freely soluble in water, 50 gms. anhydrous cobalt chloride dissolving in 100 gms. water at 15° C.

The solution behaves peculiarly when heated, changing in colour from rose at 30° C. to blue at 50° C. The red solutions appear to contain various hydrated cobalt ions, $Co(H_2O)_6^{++}$, $Co(H_2O)_4^{++}$, $Co_2(H_2O)_{10}^{++++}$, etc. The blue cobalt chloride solutions contain the

blue ions, $CoCl_4^{--}$ or $\left[\begin{matrix}Cl & & Cl \\ & Co & \\ Cl & & H_2O\end{matrix}\right]^-$ Thus cobalt chloride ionises

$$CoCl_2 \rightleftharpoons Co^{++} + 2Cl'.$$

The ion hydrates forming a red solution, *e.g.*,

$$Co^{++} + 6H_2O = Co(H_2O)_6^{++}.$$

The hydrated cation breaks up at higher temperature and a complex *anion* is formed, this having a blue colour, *e.g.*,

$$Co^{++} + 4Cl^- \rightleftharpoons CoCl_4^{--}.$$

Thus solutions of cobaltous chloride are turned blue (*a*) by heat; (*b*) by dehydrating agents, *e.g.*, alcohol; (*c*) by addition of chloride ions, *e.g.*, hydrochloric acid.

The chemical properties of cobalt chloride are those of a cobaltous salt (§ 1186), and of a chloride (§ 1057).

It forms a complex compound with ammonia, $CoCl_2.6NH_3$.

Cobalt chloride solution has been used as *invisible* or *sympathetic* ink. Words written in the pink solution are hardly visible, but on warming show up in a blue-green tint. In a few days the colour again disappears.

**1196. Cobaltic Salts.**—These are only stable in complex compounds, *e.g.*, alums, cobalticyanides, cobaltinitrites, cobaltammines, etc. The simplest stable cobaltic compound is cobalt alum,

$$(NH_4)_2SO_4.Co_2(SO_4)_3.24H_2O,$$

or cobaltic ammonium sulphate. It is made by electrolysing a solution of ammonium and cobaltous sulphates in a cell, the anode of which is enclosed in a porous pot. The cobaltous salt is oxidised at the anode to cobaltic salt,

$$Co^{++} = Co^{+++} + \ominus$$

The cobalt alum forms blue octahedra. It is a powerful oxidising agent.

**1197. Complex Compounds of Cobalt.**—A large number of *cobalt-ammines* exist. These are discussed in the section on metallic ammines (§§ 1236 *seq.*).

**1198. Detection and Estimation of Cobalt.**—Cobalt is readily detected by the blue colour it gives to the borax bead—a very delicate test.

In solution it is detected by several methods, the precipitation of potassium cobaltinitrite (§ 1192) being one of the best. The separation of nickel from cobalt analytically is best performed by Liebig's cyanide method.

The solution, containing nearly neutral nickel and cobalt salts, is treated with potassium cyanide till the precipitates redissolve.

Potassium nickelocyanide $K_2Ni(CN)_4$ is formed and also potassium cobaltocyanide $K_4Co(CN)_6$,

$$2KCN + Ni(CN)_2 = K_2Ni(CN)_4$$
$$4KCN + Co(CN)_2 = K_4Co(CN)_6.$$

The solutions are boiled and the cobaltocyanide is thereby converted into the much more stable cobalticyanide,

$$2K_4Co(CN)_6 + H_2O = 2K_3Co(CN)_6 + 2KOH.$$

Sodium hypochlorite or hypobromite (made by dissolving bromine in caustic soda) is now added. This precipitates nickel as a hydrated nickel oxide, probably $NiO_2xH_2O$, and leaves cobalt in solution.

The solution is evaporated to dryness with dilute sulphuric acid, tested, and the residue tested for cobalt by taking up in water, acidifying with acetic acid, gently warming till effervescence ceases with a solution of potassium nitrite. A yellow precipitate of potassium cobaltinitrite indicates cobalt.

Cobalt is best determined by separating it from nickel as above, precipitating it as oxide and reducing this to metallic cobalt in a current of hydrogen.

Cobalt also forms an insoluble compound with $\alpha$-nitroso-$\beta$-naphthol, nickel being unaffected. The precipitate can be washed, dried, heated to remove organic matter and the resulting oxide reduced to metal in a current of hydrogen.

## NICKEL Ni, 58·69

**1199. Historical.**—The element nickel is occasionally found in ancient coins, but it probably found its way there as a result of the smelting of copper ore containing some nickel. A mineral, known as 'kupfernickel,' or 'false copper,' 'goblin-copper,' was known in the eighteenth century. This name was given it because it resembled a copper ore in appearance but gave no copper. When Cronsted (c. A.D. 1750) first prepared a metal from this ore, he termed the new element *nickel*.

**1200. Occurrence.**—Nickel is obtained chiefly from two ores: (*a*) a deposit of iron and copper pyrites containing nickel sulphide, which occurs in very large quantities in Ontario and is now the chief source of the metal; and (*b*) an ore known as *Garnierite*, a hydrated silicate of nickel and magnesium containing some 5 per cent. of the former metal. This ore is found in New Caledonia, an island off north-east of Australia.

Nickel is found in many other minerals. Meteoric iron contains up to 20 per cent. of the metal. Nickel occurs also as arsenide and arsenate.

**1201. Extraction of Nickel from Sulphide Ores.**—The ore may be regarded as a mixture or compound of $FeS_2$, FeS, $Cu_2S$ and NiS.

The ore is separated from earthy matter and roasted in heaps or kilns. The heaps of ore are set alight by means of wood-fires and burn for two or three months. Most of the sulphur is removed, leaving crude oxides,

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$$
$$2NiS + 3O_2 = 2NiO + 2SO_2$$
$$Cu_2S + 2O_2 = 2CuO + SO_2.$$

The roasted ore is then smelted with limestone, quartz, and coke in a blast furnace, much smaller than those used for iron. By regulating the blast much of the iron is oxidised and combines with the quartz to form a slag of ferrous and calcium silicates. The metal sinking to the bottom of the furnace is an impure mixture of nickel and copper sulphides containing still some iron. This mixture is poured into a Bessemer converter with basic lining (Fig. 189) and oxidised by a blast which removes most of the sulphur and almost all the iron, a product containing some 50 per cent. of nickel, 30 per cent. of copper and 20 per cent. of sulphur remaining.

This *matte* can be used as it is for making Monel metal (§ 1205), but for most purposes is refined by various methods, the most interesting of which is the *Mond nickel process*, carried on in South Wales. The matte is roasted, yielding oxides of nickel and copper, and these are extracted with hot dilute sulphuric acid, which dissolves copper oxide readily but nickel oxide hardly at all. The copper sulphate so obtained is crystallised and sold.

The residue of nickel oxide is then reduced by water gas,

$$H_2 + NiO = Ni + H_2O.$$

This metal still contains some copper, and is refined by passing a slow stream of carbon monoxide over it at 60° C. Nickel carbonyl is produced, which is volatile.

$$Ni + 4CO = Ni(CO)_4.$$

The gas charged with the vapour of the carbonyl is passed over nickel shot heated to 180° C., where it decomposes, forming nickel and carbon monoxide, which can be used again,

$$Ni(CO)_4 = Ni + 4CO.$$

The metal produced is 99·8 per cent. pure.

Pure nickel may also be prepared by electrolysis, a process which is being rapidly developed in the U.S.A.

**1202. Properties.**—Nickel is a white and fairly soft metal, very tenacious, malleable and ductile. It has a very high melting point, 1,452° C. Its density is 8·8. Its coefficient of linear expansion is $12{\cdot}8 \times 10^{-6}$. It is perceptibly magnetic.

Nickel, like iron and cobalt, readily absorbs or dissolves hydrogen, one volume of the metal absorbing some 17 volumes of the gas.

Nickel is slowly oxidised to nickel oxide NiO in air, but burns in oxygen. Nickel is attacked by chlorine, the chloride $NiCl_2$ being formed.

Nickel is not affected by water, but at a red heat it decomposes steam. Acids do not attack it readily, except nitric acid and aqua regia. Fuming nitric acid may make it *passive* (*v.* § 1149).

Nickel is not attacked by fused caustic potash, and nickel vessels are used in the laboratory for fusing this substance.

Finely divided nickel has great catalytic power in reactions between hydrogen and other substances. In presence of nickel powder reduced by hydrogen from the oxide (the most active form of the metal) many remarkable reductions can be carried out. A mixture of nitric oxide and hydrogen yields ammonia,

$$5H_2 + 2NO = 2H_2O + 2NH_3.$$

A mixture of ethylene and hydrogen yields ethane,

$$C_2H_4 + H_2 = C_2H_6.$$

This method of reduction, introduced by Sabatier and Senderens, has been found particularly useful in organic chemistry. Many inedible liquid oils may be converted into useful hard fats suitable for margarine making, by adding to them a little finely-divided nickel and bubbling hydrogen through them at about 250° C. The oils used contain the unsaturated grouping $\begin{matrix}—C— \\ \| \\ —C—\end{matrix}$ which is converted by hydrogen into $\begin{matrix}—CH— \\ | \\ —CH—\end{matrix}$.

The explanation of the catalytic action of finely-divided nickel appears doubtful, but probably depends on the fact that nickel adsorbs both hydrogen and the substance to be reduced.

**1203. Uses of Nickel.**—Nickel is used as a catalyst, as already explained, but finds a more considerable use in electro-plating and in the making of certain alloys.

**1204. Electro-plating.**—Nickel being white, lustrous, hard and almost unaffected by air and moisture, is suitable for covering other cheaper metals which have not these advantages.

The apparatus consists of a plating bath containing a solution of nickel ammonium sulphate (375 gms.), nickel sulphate heptahydrate (100 gms.), water (5 litres). The anodes are bars of cast nickel of

high purity. The articles to be plated are highly cleaned and form the cathodes. A current of 2·5 amps. per square decimetre of cathode is suitable at a temperature of about 50° C. The nickel sulphate decomposes,

$$NiSO_4 = Ni \rightarrow \text{cathode} + SO_4 \rightarrow \text{anode},$$

and the liberated sulphate groups attack the anodes, reproducing the nickel sulphate used up.

**1205. Alloys.**—Nickel is used for various foreign coinages, but its alloys with copper are preferred. The chief alloys of nickel are :—

(*a*) Nickel steels, invar, platinite, etc.
(*b*) Copper-nickel alloys, Monel metal, cupro-nickel, nickel bronze.
(*c*) Copper-nickel-zinc alloys, nickel silver.
(*d*) Copper-nickel-zinc-silver. British coinage alloy before 1946.
(*e*) Nickel-chromium alloy.

(*a*) Nickel steels containing some 2½ to 5 per cent. of nickel are of great toughness and elasticity and find considerable use for structural work, crank-shafts, gears, heavy guns, etc.

Nickel steel containing 35 per cent. of nickel with a little manganese and carbon is known as *invar*, and is valuable as having a negligible coefficient of expansion. It is useful for making pendulum rods, etc. *Platinite* contains about 46 per cent. of nickel and has the same coefficient of expansion as platinum and glass and can be used for sealing wires into glass apparatus, such as electric lamp bulbs. Copper-coated nickel wire is now chiefly used for this purpose.

(*b*) Several alloys of nickel and copper are in use. Cupro-nickel, containing 20 per cent. of nickel, is used for bullet jackets. The white coinage alloy containing 25 per cent. of nickel and 75 per cent. copper is extensively used in Europe and America. Hence the term ‘ a nickel,’ which in America denotes a 5-cent piece. Monel metal is a very tough alloy of high melting point (1,360° C.). It contains about 60 per cent. nickel, the remainder being some 33 per cent. of copper and 7 per cent. of iron. It is used for propellers of ships, blades of turbines, pumps and boilers, and in Germany for locomotive fire-boxes. It is resistant to attack by chemical reagents and finds some uses on this account.

(*c*) Nickel silver, also known as German-silver, contains from 50 to 60 per cent. of copper, 10 to 30 per cent. of nickel, and 20 to 35 per cent. of zinc. It is used for all manner of cheap white metal goods, spoons, forks, fancy goods, etc. It is largely used as a basis for electroplate (§ 309).

(*d*) British coinage alloy. This contains 5 per cent. of nickel : Ag, 50 per cent. ; Cu, 40 per cent. ; Zn, 5 per cent. ; Ni, 5 per cent. (Up to 1946 only.)

(*e*) Ni-chrome, containing 60 per cent. nickel and about 15 per cent. each of iron and chromium, is used for the resistance wire for the windings of electric furnaces. It is very resistant both to heat and to chemical reagents and has been used for machine parts which have to withstand high temperatures.

**1206. Atomic Weight of Nickel.**—Similar methods and reasoning to that used in the case of cobalt indicate a value for the atomic weight of 58·69.

**1207. Nickel Oxides.**—The unquestioned oxides of nickel are :—

| | |
|---|---|
| Nickelous oxide . . . . . | $NiO$ |
| Nickelonickelic oxide . . . . | $Ni_3O_4$ |
| Nickel dioxide . . . . . | $NiO_2$ |

A sesquioxide, $Ni_2O_3$, is often referred to but is probably a mixture of $NiO$ and $NiO_2$. Of these oxides the first is the only one commonly met with. There is some evidence of the existence of higher oxides.

**1208. Nickelous Oxide.**—This oxide is obtained by the usual methods from nickelous salts or by heating nickel to a red heat in steam.

Pure nickel oxide is a green solid, unaffected by heat. It is reduced by hydrogen and carbon monoxide at about 200° C. or lower. It is a basic oxide and has no acidic properties.

**1209. Nickelous Hydroxide $Ni(OH)_2$** is also obtained by the usual methods. It forms a green precipitate soluble in ammonia to a lavender-blue solution, containing the ion $Ni(NH_3)_6^{++}$. It is basic in character, forming salts with acids.

*Nickelo-nickelic oxide* $Ni_3O_4$ is known.

**1210. Nickel Dioxide** is obtained as a black hydrate, $NiO_2.xH_2O$, when a nickel salt is treated with sodium hypochlorite solution,

$$NiCl_2 + NaOCl + 2NaOH = NiO_2.H_2O + 3NaCl.$$

This reaction is used in the *cyanide method* of separating nickel and cobalt (§ 1198). The oxide behaves chemically very much like manganese or lead dioxide. Thus with hydrochloric acid it gives chlorine,

$$NiO_2 + 4HCl = NiCl_2 + 2H_2O + Cl_2,$$

and a nickelous salt. With sulphuric acid

$$2NiO_2 + 2H_2SO_4 = 2NiSO_4 + 2H_2O + O_2,$$

oxygen and a nickelous salt result.

**1211. Nickel Salts.**—Nickel forms only one series of soluble salts, the *nickelous* salts, in which the metal is divalent. There is some evidence of the existence of nickelic compounds in which the metal is trivalent, but the salts, if existent, are too unstable to be isolated. The nickel ion ($Ni^{++}$) has a pseudo-inert-gas structure with eight outer electrons (p. 750). This fact makes it particularly stable, and accordingly nickel does not lose further electrons and so exhibit a valence of 3 or more.

Nickel salts are prepared by the usual methods from the oxide, hydroxide, or carbonate. The metal is not easily attacked by most acids, but the nitrate is made from it by the use of nitric acid.

If nickel salts are required quite free from cobalt they are best prepared by precipitating all cobalt as potassium cobaltinitrite (§ 1192) and preparing nickel hydroxide by the action of ammonia

on the resulting solution. This may be well washed, dried and converted into the salt required.

Nickel salts are yellow when anhydrous and green when hydrated or in solution. With ammonia they give a pale green precipitate, soluble in excess of the reagent to a blue solution (*v.* § 1209). With hydrogen sulphide in alkaline or neutral solution black nickel sulphide NiS is deposited. Like ferrous salts they absorb nitric oxide, but unlike them do not form a coloured compound.

**1212. Nickel Carbonate.**—Basic nickel carbonates,

$$NiCO_3.nNi(OH)_2,$$

are obtained when sodium or potassium carbonates react with solutions of nickel salts. The normal carbonates can be obtained by special methods. They form light green powders, which readily decompose when heated, giving nickel oxide.

**1213. Nickel Nitrate $Ni(NO_3)_2$** is met with as the hexahydrate, $Ni(NO_3)_2.6H_2O$, which is prepared by the usual methods (§ 172). It forms green crystals, very soluble in water. At 20° C. water dissolves half its own weight of the anhydrous salt.

The hexahydrate loses some water of crystallisation and then decomposes before it becomes anhydrous,

$$2Ni(NO_3)_2 = 2NiO + 4NO_2 + O_2.$$

It is thus impossible to make the anhydrous salt by heating the hydrate. The anhydrous salt has been made by the action of nitrogen pentoxide on the hydrated salt,

$$Ni(NO_3)_2.6H_2O + 6N_2O_5 = Ni(NO_3)_2 + 12HNO_3.$$

**1214. Nickel Monosulphide NiS** is obtained when hydrogen sulphide acts on nickel salts in presence of alkalis. It exists in three forms: $\alpha$-nickel sulphide is readily soluble in acids, $\beta$-nickel sulphide dissolves in moderately dilute acid ($2N$.HCl), and $\gamma$-nickel sulphide is not attacked by acids.

The $\alpha$-form is first produced when nickel sulphide is precipitated, but it quickly changes to the $\gamma$-form. Thus we account for the peculiar fact that although nickel sulphide is not precipitated in acid solution, yet, when precipitated in alkaline solution, it is insoluble in hydrochloric acid, particularly after boiling. This fact is utilised in qualitative analysis.

Several other sulphides, $Ni_2S_3$, $Ni_3S_4$, $NiS_2$, $NiS_4$, are said to exist.

**1215. Nickel Sulphate $NiSO_4$** is the best known salt of nickel. It may be prepared by the usual methods (§ 172). The usual form met with is the *heptahydrate* $NiSO_4.7H_2O$. This forms green crystals, while the *hexahydrate* $NiSO_4.6H_2O$ is blue. The anhydrous salt is yellow.

When heated it forms nickel monoxide,

$$NiSO_4 = NiO + SO_3.$$

It has the usual properties of nickel salts and sulphates. Nickel sulphate forms a compound with ammonia gas, $Ni(NH_3)_6SO_4$. If anhydrous nickel sulphate is dissolved in concentrated ammonia solution an unstable dark blue salt is formed, nickelammonium sulphate, $Ni(NH_3)_4SO_4.2H_2O$, analogous to cuprammonium sulphate (§ 286). This should be carefully distinguished from nickel ammonium sulphate, $NiSO_4.(NH_4)_2SO_4.6H_2O$, which is a stable salt analogous to ferrous ammonium sulphate. The latter salt is used in electro-plating (§ 1204).

**1216. Nickel Chloride $NiCl_2$** may be prepared by the usual methods. The anhydrous salt may be prepared by the action of chlorine on finely divided nickel.

Nickel chloride is yellow when anhydrous. It is usually met with as the hexahydrate, $NiCl_2.6H_2O$. The salt is very soluble in water, 100 gms. of the solution containing 39·1 gms. $NiCl_2$ at 20° C.

When heated in air nickel chloride gives chlorine and the oxide

$$2NiCl_2 + O_2 = 2NiO + 2Cl_2.$$

Like most metallic chlorides the anhydrous salt forms a loose compound with ammonia, $NiCl_2.6NH_3$. Among the double salts formed by it *nickel ammonium chloride*, $NiCl_2.NH_4Cl.6H_2O$, is the best known.

**1217. Nickel Carbonyls.**—Like iron and cobalt nickel forms a *carbonyl*. Nickel tetracarbonyl is readily made by reducing nickel oxide to metallic nickel at 400° C. in a stream of hydrogen, and passing a stream of carbon monoxide over the metal warmed to 30°–50° C.

$$Ni + 4CO = Ni(CO)_4.$$

The carbonyl is condensed in a well-cooled vessel.

Nickel carbonyl is a colourless and extremely poisonous liquid boiling at 43° C. When heated it decomposes, giving nickel and carbon monoxide,

$$Ni(CO)_4 = Ni + 4CO.$$

Its use in the industrial purification of nickel has been described in § 1201.

**1217a. The Metallic Carbonyls.**—Carbonyls of the type $M(CO)_n$ where M is a metal are formed by numerous metals. They are of two types :—

(1) Solid non-volatile carbonyls formed by the alkali metals. The explosive potassium carbonyl is an example.

(2) Volatile carbonyls. These are formed by copper, chromium, molybdenum, tungsten, iron, ruthenium, rhodium, osmium, cobalt and nickel.

The following is a list of formulæ of these carbonyls : $Cr(CO)_6$, $Mo(CO)_6$,

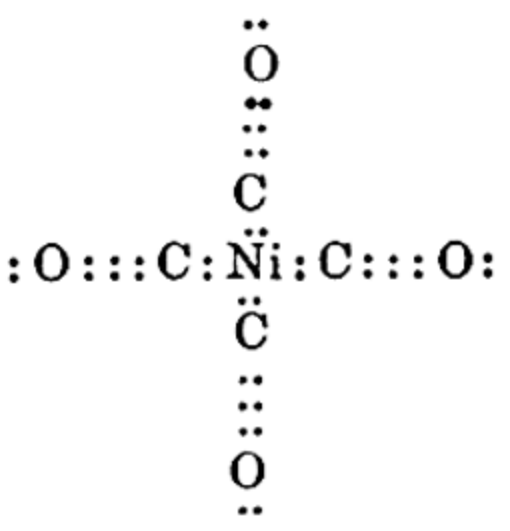
$W(CO)_6$, $Co_2(CO)_6$, $Co_4(CO)_{12}$, $Ni(CO)_4$, $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Cu(CO)_3$, $[Rh(CO)_4]_2$, $Rh_4(CO)_{11}$, $Ru(CO)_5$, $Ru_2(CO)_9$, $Os(CO)_5$, $Os_2(CO)_9$. It is noticeable that analogous elements have carbonyls of the same type of formula.

These carbonyls are formed either by the action of carbon monoxide, best compressed, on the metal, or by the action of heat on other carbonyls.

They are obviously covalent, being soluble in organic solvents, and volatile at fairly low temperatures. They are all decomposed by heat, ultimately forming the metal and carbon monoxide.

The carbonyl groups may be replaced in some cases by nitrosyl groups NO.

Much light has recently been thrown upon the structure of the metallic carbonyls (§ 1172, 1188, 1217). Those carbonyls which contain but one atom of metal contain as many molecules of carbon monoxide as, by donating two electrons apiece, will serve to bring the number of electrons contained in and shared by the metal atom up to the number possessed by the inert gas which follows it in the Periodic table. Carbon monoxide : O : : : C : can donate two electrons to a single metal atom ; a nickel atom has 28 electrons ; a krypton atom 36. Accordingly, the nickel atom in nickel carbonyl requires 36 − 28 = 8 electrons, and combines with four molecules of carbon monoxide. The formula of nickel carbonyl is $Ni(CO)_4$, and its structure is



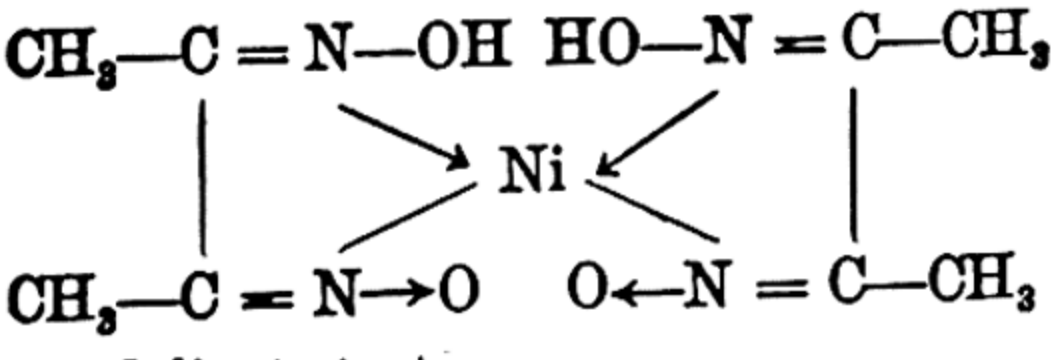
From the rule also follows the formulæ $Fe(CO)_5$ and $Cr(CO)_6$. No compound $Mn(CO)_n$ or $Co(CO)_n$ could be formed if the above rule is correct, for these metal atoms would need an odd number of electrons.

**1218. Detection and Estimation of Nickel.**—Nickel salts are green in solution, and with ammonia their solutions give a pale green precipitate, redissolving to a blue solution,

$$Ni^{++} + 2OH^- \rightleftharpoons Ni(OH)_2\downarrow$$
$$Ni^{++} + 6NH_3 \rightleftharpoons Ni(NH_3)_6{}^{++}.$$

It is detected in presence of much cobalt by Liebig's cyanide method (§ 1198) or by the addition to the nearly neutral or alkaline solution a solution of α-dimethyl-glyoxime or α-diphenyl-glyoxime.

The former reacts with nickel salts giving a scarlet precipitate of composition



and affords a very delicate test.

*Estimation.*—The precipitate obtained by the use of the glyoxime may be filtered off, dried at *c.* 110° C. and weighed as such, or may be ignited and weighed as nickel oxide.

There is also a volumetric method employing potassium cyanide.

## RUTHENIUM, RHODIUM, PALLADIUM

These three metals form the second set of transition elements. The first two elements are very rare, but palladium is commoner and finds some commercial applications.

**1218a. The Platinum Metals.**—Ruthenium, rhodium, palladium, osmium, iridium and platinum are found native as alloys, chief of which are crude platinum found in Colombia and Russia, and osmiridium found in Tasmania. However, half of the world's production of these metals now comes from the treatment of the residues from Canadian nickel manufacture

The separation of these metals is a difficult task, and is best expressed as a table. The ore is boiled with acid to remove base metals and impurities, then treated with aqua regia. Part dissolves and part is unattacked.

<table>
<tr><td colspan="2">A. Undissolved.<br>Osmium, most of the Iridium, some of the Ruthenium.<br>Heat in a stream of oxygen and condense volatile substances evolved.</td><td colspan="3">B. Dissolved.<br>Platinum, Palladium, Rhodium, some Iridium and Ruthenium, as higher chlorides.<br>Evaporate to dryness and heat gently. Platinum and iridium give lower chlorides. Dissolve in very dilute HCl and add $NH_4Cl$.</td></tr>
<tr><td>Condensed</td><td>Residue</td><td>Solution</td><td colspan="2">Precipitate</td></tr>
<tr><td>Pass $Cl_2$ through hot acidified solution. Osmium tetroxide volatilises and ruthenium tetroxide remains.</td><td>Iridium. Dissolve in aqua regia and add to the dissolved metals. (Right-hand column B)</td><td>Rhodium, Ruthenium and Palladium chlorides. Precipitate metals with iron. Dissolve in aqua regia, concentrate; add ammonium chloride.</td><td colspan="2">Ammonium chloroplatinite and chloroiridite, $(NH_4)_2PtCl_4$ and $(NH_4)_2IrCl_4$.<br>Ignite precipitate forming metals. Iridium is not usually separated from platinum; but if this is required a separation may be based on the fact that Ir is less easily dissolved by aqua regia than is Pt.</td></tr>
<tr><td></td><td></td><td>Solution</td><td>Precipitate</td><td></td></tr>
<tr><td></td><td></td><td>Evaporate to dryness. Ignite. Fuse with $KHSO_4$. Treat with water.</td><td>Diamminopalladous chloride $(NH_3)_2PdCl_2$.<br>Heat to redness.<br>↓<br>Metallic Palladium.</td><td></td></tr>
<tr><td></td><td></td><td>Solution</td><td>Precipitate</td><td></td></tr>
<tr><td></td><td></td><td>Potassium Rhodium Sulphate.</td><td>Ruthenium metal.</td><td></td></tr>
</table>

## RUTHENIUM Ru, 101·7

**1219. Ruthenium and Its Compounds.**—Ruthenium is found with platinum (*q.v.*) It is a hard grey brittle metal. Like palladium it absorbs

gases. It is oxidised by oxygen to the dioxide $RuO_2$ and the volatile tetroxide $RuO_4$ (cf. Osmium, p. 786).

Ruthenium is not attacked by acids, and only slowly by chlorine.

Ruthenium appears to have the valencies, 2, 3, 4, 6 and 8, but the first is doubtful.

*Oxides of Ruthenium.*—There is some doubt as to what oxides of this metal really exist, but $Ru_2O_3$, $RuO_2$ and $RuO_4$ are certainly known. The oxides appear to have feeble basic properties, but form well-marked *ruthenates*, $M_2RuO_4$, and *per-ruthenates*, $MRuO_4$.

*Chlorides of Ruthenium.*—Ruthenium forms two chlorides, $RuCl_2$ and $RuCl_3$. The former has not been prepared pure, but the latter is stable enough to be prepared in a pure state. Solutions of the chloride hydrolyse very easily. Chlor-ruthenites and chlor-ruthenates exist, $M_2'RuCl_5$ and $M_2'RuCl_6$ (analogous to the chloroplatinates).

*Ruthenium sulphate* $Ru(SO_4)_2$ exists.

## RHODIUM Rh, 102·91

**1220. Metallic Rhodium.**—Rhodium is obtained from platinum ores (*q.v.*). It is a white lustrous metal of very high melting point (1,907° C.). It is slightly oxidised when heated in air, probably forming the sesquioxide $Rh_2O_3$. Chlorine attacks it, but acids are without effect. Rhodium does not absorb gases so freely as ruthenium or palladium. Rhodium black has great catalytic powers (*v.* platinum black, § 1228).

Rhodium has found a use in thermocouples, and is sometimes alloyed with platinum in order to increase its hardness. Rhodium plating is sometimes adopted in place of silver plating. The metal closely resembles silver, but is hard and untarnishable.

**1221. Compounds of Rhodium.**—*Rhodium oxides.*—Several oxides of rhodium exist. Rhodium sesquioxide $Rh_2O_3$ is basic, giving rhodium salts with acids. Rhodium dioxide is probably (like lead dioxide) a basic oxide with unstable salts. Rhodium trioxide is acidic in character, forming rhodates, $M_2'RhO_4$.

*Rhodium trichloride* $RhCl_3$ is a red solid. It exists in an insoluble and a soluble form, resembling chromic chloride in this respect. It forms double salts with alkali chloride, hexachlorrhodites $M_3'RhCl_6$, and pentachlorrhodites $M_2'RhCl_5$.

*Rhodium sulphate* $Rh_2(SO_4)_3$ is known and forms a well-marked alum known as ammonium rhodium alum,

$$(NH_4)_2SO_4.Rh_2(SO_4)_3.24H_2O.$$

*Rhodium nitrate* $Rh(NO_3)_3.2H_2O$ is also known.

## PALLADIUM Pd, 106·7

**1222. Metallic Palladium.**—Palladium is prepared from platinum residues (§ 1228) or from certain nickel ores.

It is obtainable, like platinum (*q.v.*), as compact metal, 'sponge' and 'black.'

Palladium is a white metal, much resembling platinum. It melts at 1,550° C. The most remarkable property of palladium is its power of absorbing hydrogen, and to a lesser degree other gases. A piece of palladium foil, which has been heated in a vacuum to

remove other gases, absorbs up to 936 times its volume of hydrogen, increasing somewhat in volume during the process. It has been thought that a palladium hydride, $PdH_2$ or $Pd_2H$, may be formed, but there is much evidence against this. It is found that the amount of hydrogen absorbed depends on the temperature and pressure, and the palladium-hydrogen system obeys Henry's law (p. 93).

It is probable that the hydrogen is actually dissolved in the palladium, but in order to avoid begging the question the term *occlusion* is applied to this type of gas absorption.

The *occluded* hydrogen is more reactive chemically than free hydrogen, and has the reducing power of *nascent* hydrogen (§ 192).

Hydrogen can pass freely through heated palladium. Thus, if hydrogen be passed through a palladium tube it will pass out through the walls at the rate of about 4 c.c. per minute per 100 sq. cm., at a temperature just below red heat. There is some evidence based on the rate of diffusion that the hydrogen dissociates into single atoms in passing through the metal.

Palladium has remarkable catalytic powers, similar in character to those of platinum. Thus, at 280° C., hydrogen and oxygen combine to form water in presence of palladium foil, and palladised asbestos (*v.* § 1228) will cause hydrogen to be oxidised to water even in the cold. The oxidation of hydrocarbons is also catalysed, though less effectively.

*Chemical Properties.*—Palladium is oxidised when heated to redness in oxygen. Chlorine attacks heated palladium, forming the chloride. Hydrochloric acid, nitric acid, and sulphuric acid, when heated, attack the metal.

**1223. Compounds of Palladium.**—*Oxides of Palladium.*—The oxides PdO, $Pd_2O_3$ and $PdO_2$ exist.

*Palladous oxide* PdO is basic in character. When heated it decomposes in a reversible manner.

$$2PdO \rightleftharpoons 2Pd + O_2.$$

It is very readily reduced by hydrogen.

*Palladium dioxide* $PdO_2.xH_2O$ is unstable, readily decomposing to the monoxide at temperatures above 100° C.

*Salts of Palladium.*—Palladium forms a series of palladous salts, in which the metal is divalent. They are readily reduced to metallic palladium when heated. Palladic salts in which palladium is trivalent are unstable, but like cobaltic salts (§ 1196) form stable complexes.

*Palladous chloride* $PdCl_2$ is made by the action of chlorine on the metal and forms red crystals. It is decomposed when heated to the metal and chlorine.

Various *chlorpalladites*, as $(NH_4)_2PdCl_4$, ammonium chlorpalladite, are known.

*Palladium trichloride* $PdCl_3$ and palladium tetrachloride $PdCl_4$ do not exist, but pentachlorpalladates $M_2PdCl_5$ and hexachlorpalladates $M_2PdCl_6$ are known.

*Palladous sulphate* $PdSO_4.2H_2O$ exists, as also does palladous nitrate $Pd(NO_3)_2$.

*Uses.*—Palladium alloyed with gold has been used as a platinum substitute, and the metal has sometimes been used for articles of jewellery. It has the colour and incorrodibility of platinum, while being considerably cheaper. It is not, however, so resistant to chemical action as the latter metal, and cannot replace it in scientific apparatus.

## OSMIUM, IRIDIUM, PLATINUM

Osmium, iridium and platinum form the heaviest of the three sets of elements of Group VIII. of the Periodic table. They resemble each other in their high melting point and density and in the relative instability of their compounds, which is most noticeable in platinum and least in osmium.

### OSMIUM Os, 190·2

**1224. Metallic Osmium.**—Osmium is found alloyed with iridium as *osmiridium*, found in small grains in certain sands in South America, the Urals, Tasmania, etc. It contains as a rule 50 to 70 per cent. of iridium and 30 to 40 per cent. of osmium, with varying amounts of rhodium, platinum and ruthenium.

Osmium is isolated from osmiridium by alloying it with zinc, crushing it and heating with an oxidising agent ($BaO_2$) and treating with hydrochloric acid. The solution is distilled, and a solution containing the volatile osmium tetroxide $OsO_4$ comes over. Hydrogen sulphide converts this into the insoluble sulphide $OsS_4$, which, when strongly heated in a closed carbon crucible, yields metallic osmium.

*Properties.*—Osmium is a very hard, brittle metal of extremely high density, 21·3 to 24. The latter figure represents the highest density of any substance existing on earth. A piece of osmium the size of two common bricks would weigh as much as 180 lbs. and would need a strong man to lift it.

It has a very high melting point, *c.* 2,700° C. It is remarkable as being readily oxidised, resembling in this respect ruthenium and iron, its vertical neighbours in the Periodic table, rather than iridium and platinum.

When heated in air to a temperature of about 200° C. it forms the remarkable volatile tetroxide, $OsO_4$. It is oxidised by nitric acid, and chlorine also attacks it, forming $OsCl_4$.

Finely divided osmium has effective catalytic power for many reactions, including that of the synthesis of ammonia (§ 689).

Osmium has found a use in electric light filaments, being only less infusible than tungsten.

**1225. Oxides of Osmium.**—Four oxides, OsO, $Os_2O_3$, $OsO_2$ and $OsO_4$, exist. The last only need be mentioned here.

*Osmium tetroxide* $OsO_4$, sometimes called osmic acid, is made by oxidising the metal by heating in air or with nitric acid.

It is a solid, melting at 45° C. and subliming when gently heated. It has a penetrating smell and the vapour is intensely poisonous. Its vapour density shows the formula $OsO_4$ to be correct.

The oxide is remarkable, firstly, in its volatility and, secondly, in the fact that ruthenium tetroxide, osmium tetroxide, osmium tetrasulphide $OsS_4$, and

osmium fluoride $OsF_8$ are the only examples of octavalency. It is not an acidic oxide.

It is readily reduced to metallic osmium, and is used as a microscope stain, being reduced by fatty substances to black metallic osmium.

*Osmium octafluoride* $OsF_8$ is a volatile solid of low melting point, 45° C. It boils at 100° C. The low boiling point indicates that it is not a salt but a covalent compound. A hexafluoride, $OsF_6$, is also known.

*Osmium dichloride*, *trichloride* and *tetrachloride* all exist and orm double salts, such as *potassium chlorosmate* $K_2OsCl_6$.

Osmium forms no salts with oxyacids. The so-called osmyl salts contain the osmium in the acid radical, *e.g.*, potassium osmylnitrite $K_2[OsO_2(NO_2)_4]$.

Metallic atoms never form ions in which a higher valency than three (or rarely four) is displayed.

## IRIDIUM Ir, 193·1

**1226. Metallic Iridium.**—Iridium is found alloyed with platinum or osmium and is extracted by the method explained under the heading of platinum (§ 1228).

Iridium is a hard brittle white metal. Its density is 22·4 and its melting point 2,290° C.

Iridium is extremely resistant to chemical action. Even fluorine does not attack it below a red heat. Chlorine attacks it at a red heat, but acids have no action upon it. It may, however, be dissolved by treatment with fused caustic potash and potassium nitrate, so forming *iridates*.

Iridium finds uses, especially when alloyed with platinum, for apparatus required to be strong and completely incorrodible. The standard metre is composed of platinum iridium alloy. The tips of fountain pen nibs have been made from natural granules of iridium-platinum alloy, but the very high price of the metal has led to the common use of tungsten alloys for this purpose.

**1227. Compounds of Iridium.**—Iridium forms several oxides, $Ir_2O_3$, $IrO_2$, $IrO_3$, the latter existing only in its salts, *e.g.*, $K_2IrO_4$. When heated in air they all decompose readily into the metal and oxygen.

The sesquioxide $Ir_2O_3$ is basic and the dioxide appears to be acidic in character.

Several iridium chlorides are known but the usual one is the trichloride $IrCl_3$. It is obtained by heating the metal to redness in chlorine. It is insoluble in water.

Potassium chloriridite $K_3IrCl_6$ and chloriridate $K_2IrCl_6$ are known.

*Iridium sulphate* $Ir_2(SO_4)_3$ can be obtained as a yellow substance.

*Iridium alum* $K_2SO_4 . Ir_2(SO_4)_3 . 24H_2O$ can also be made.

Various complex iridium compounds, iridinitrites, iridicyanides, etc., analogous to the cobalt and platinum compounds (§§ 1236 *seq.*) are known.

## PLATINUM Pt, 195·23

**1228. Occurrence and Extraction.**—Platinum occurs native alloyed with more or less of the other platinum metals. It is found in quantity in Russia, the chief source, and also in British Columbia. Platinum occurs as a rule in alluvial sands and gravels and is found

in grains, or nuggets which have been known to weigh 20 lbs. The very dense grains are separated by washing the alluvium, and the crude platinum is refined.

It is first digested with *aqua regia* which dissolves all but the *osmiridium*, which is treated separately (§ 1224). The solution of the chlorides of platinum, palladium, etc., is then treated with ammonium chloride and yellow insoluble ammonium chloroplatinate $(NH_4)_2PtCl_6$ is precipitated. A little ammonium chloriridate also comes down. The salt is then heated, when platinum is left behind,

$$(NH_4)_2PtCl_6 = Pt + 2NH_4Cl + 2Cl_2.$$

The metal, which is left in the spongy state, is usually redissolved and reprecipitated as chloroplatinate to remove all traces of iridium, and the platinum resulting from its decomposition is fused in an oxyhydrogen furnace. The last traces of iridium are difficult to remove, but for most purposes its presence is immaterial, or even desirable, as it makes the metal harder and less corrodible.

Beside the ordinary compact metal, platinum can be prepared as platinum sponge, platinum black and colloidal platinum. Platinum sponge is made by heating ammonium chloroplatinate. It forms a soft and porous mass. Its large surface makes it a vigorous catalyst (*v. infra.*)

Platinum black is very finely divided platinum, prepared by reducing platinum chloride with various reducing agents, sodium formate or alkaline glucose solution being suitable.

It forms a black powder with great catalytic activity.

Colloidal platinum is best made by Bredig's method (§ 92 (2) ). Colloidal platinum has very considerable catalytic activity (p. 797).

Platinised asbestos is obtained by soaking asbestos in platinum chloride solution and decomposing the salt by heating it to about 500° C. Platinum in this form presents a very great surface.

**1229. Properties.**—Platinum is a white metal of silvery lustre. It is strong and readily worked. It melts at *c.* 1,754° C. Platinum has a density of 21·4. Its coefficient of linear expansion is very low, being 0·0000089 between 0° C. and 100° C. Soft glass has a coefficient of expansion of about 0·0000085, and so platinum can be sealed into glass without any fear of uneven expansion damaging the joint. This is a most valuable property from the point of view of the scientific instrument maker.

Platinum absorbs hydrogen, but not to a very great extent.

*Chemical Properties.*—Platinum is not oxidised when heated, but the heated metal is attacked by fluorine and chlorine.

Acids do not attack platinum to any appreciable extent. Boiling sulphuric acid has a very slight action.

Aqua regia, or any mixture evolving chlorine, attacks platinum, yielding hexachloroplatinic acid.

$$2HCl + Pt + 2Cl_2 = H_2PtCl_6.$$

Platinum is affected by carbon. Thus a smoky luminous coal-gas flame renders a platinum crucible brittle, and a luminous flame should not be allowed to touch platinum. It alloys easily with lead, and therefore it should not be soldered nor should lead compounds be heated in contact with it.

*Platinum as a Catalyst.*—The metallic platinum has remarkable catalytic activity, especially in gas reactions. We may mention among reactions which are accelerated by the presence of platinum the following :—

Combination of oxygen and hydrogen (§ 189).
Oxidation of ammonia (§ 738).
Reduction of nitric oxide to ammonia (§ 715).
Combination of bromine and iodine with hydrogen (§§ 1078, 1094).
Reduction of hydrocyanic acid to methylamine.
Oxidation of sulphur dioxide to sulphur trioxide (§ 930).
Oxidation of methyl alcohol to formaldehyde.
Decomposition of hydrogen peroxide (§ 214).
Reaction of carbon monoxide and oxygen.
Reaction of hydrogen with ferric salts, acetylene, ethylene.
Decomposition of hydrazine hydrate.

This list is not complete, but serves to show what a varied list of reactions is affected by this metal. The surface-action theory of catalysis is clearly applicable to these reactions, for no intermediate compound theory could well be applied to such an unreactive metal as platinum.

The mechanism of these processes is discussed in §§ 108, 109, but, shortly, it may be said that the activity of platinum is due to its adsorbing or condensing on its surface a highly concentrated layer of the reacting compounds, bringing thereby the molecules into close proximity.

The fact that the catalytic activity of platinum is a surface action is demonstrated by the difference of activity of its various forms. It is found that the more finely divided is platinum the greater is its catalytic activity. Thus compact freshly-heated platinum, wire or foil, will bring about the combination of hydrogen and oxygen or the oxidation of methyl alcohol or the oxidation of ammonia. Platinum black, of which the particles are very small, causes hydrogen to combine with oxygen explosively and will cause alcohol to oxidise in

air to acetic acid. Colloidal platinum causes hydrogen and oxygen to unite even in the cold, while the decomposition of hydrogen peroxide is influenced by the presence of as little as ·000000001 gm. of platinum in the colloidal state per cubic centimetre of liquid.

The reason of this difference lies in the *surface* of the various forms. A cube of platinum of volume 1 c.c. has a surface of 6 sq. cm. If we imagine this cube divided into cubic particles the length of the edges of which were $10^{-3}$ cm., each of these would have a surface of $6 \times 10^{-6}$ sq. cm., and as there would be $10^9$ of them the total surface of the platinum would be 6,000 sq. cm. In colloidal platinum the particles are invisible under the most powerful microscope and may approximate to a diameter of $10^{-6}$ cm. In this state (assuming the particles to be cubes) the surface of 1 c.c. of platinum would be $6 \times 10^{-12} \times 10^{18} = 600$ square metres.

**1230. Uses of Platinum.**—The chief uses of the metal are for chemical, electrical, dental and ornamental purposes.

For chemical apparatus platinum is invaluable in that it is unaffected by most chemical reagents, and is unaltered by the highest degree of heat (*c.* 900–1,000° C.) used in ordinary chemical operations. It is, however, perceptibly attacked by alkalis and free metals. A platinum crucible keeps the same weight to a tenth of a milligram during months of use. Platinum wire does not melt in the Bunsen flame and does not colour it, and it is accordingly used for flame tests in qualitative analysis. The very high price of platinum has led to a search for substitutes both in this field and others, but nothing wholly satisfactory has been found. Certain alloys of cast iron, containing silicon, have replaced platinum for large vessels used for the concentration of sulphuric acid and for certain operations where an incorrodible metal is required. Fused quartz has also been largely used, but has the disadvantage of being easily attacked by alkalis.

The use of platinum as a catalyst in chemical industry is an important one.

In electrical work platinum has the advantage of being readily sealed into glass and also of being practically non-volatile and unoxidised by air. It is unequalled for the contacts of relays, etc., where sparking may take place. Other metals become oxidised and their use leads to the contacts failing, and their volatility causes arcing to take place. Platinum is almost non-volatile, and accordingly the sparks produced are smaller, and though the metal may become disintegrated by sparking, it none the less remains bright and conductive.

Platinum is occasionally used to make dental plates and the pins which hold false teeth in position. Its usefulness is due to its strength and its incorrodibility. Teeth are sometimes filled with

the metal. As much as a ton of platinum is used yearly for this purpose. A ton of platinum would go into a good-sized suitcase and is worth nearly half a million pounds.

Platinum is used in jewellery, its silvery-grey colour looking very well with diamonds. Its high cost is perhaps an additional attraction. Platinum salts are used in the platinotype process of photography, which yields very beautiful and probably completely permanent images.

The alloys of platinum are not very important. Its alloy with iridium (§ 1226) is valuable for standard weights and measures, being strong and incorrodible. Gold alloyed with a little platinum and silver alloyed with platinum are used in dentistry.

**1231. Atomic Weight of Platinum.**—Dulong and Petit's law leads to a value of 198 for the atomic weight, a value in agreement with its natural position in the Periodic table. The exact value results from a number of accurate determinations, including amongst many others the determination of the weight of platinum obtained from a given weight of potassium platinichloride $K_2PtCl_6$. The value 195·2 is accepted.

**1232. Oxides of Platinum.**—The oxides, PtO, $Pt_2O_3$, $PtO_2$, $PtO_3$, exist.

*Platinous oxide* PtO is prepared in a hydrated condition by the action of caustic potash on platinous chloride. It is basic in character. It is oxidised by air to platinum dioxide, though it is itself a powerful oxidising agent. Heat decomposes it to platinum and oxygen.

The other oxides of platinum are also strong oxidising agents. Heated, they decompose, yielding the metal and oxygen.

**1233. Platinum Halides.**—Three well-marked platinum chlorides exist, $PtCl_2$, $PtCl_3$, $PtCl_4$.

*Platinous chloride* $PtCl_2$ is made by carefully heating the tetrachloride at about 300°–350° C.,

$$PtCl_4 = PtCl_2 + Cl_2.$$

It forms double salts, known as tetrachlorplatinites. All the chlorides of platinum appear to form complex acids with hydrochloric acid. Tetrachlorplatinous acid is unstable, but the salts, $K_2PtCl_4$, etc., are well known, the latter being a red-brown well-crystallised salt.

*Platinum trichloride* $PtCl_3$ is made by carefully regulated heating of the tetrachloride. It is readily decomposed into the di- and tetrachloride.

*Platinic chloride, platinum tetrachloride* $PtCl_4$, is obtained by the heating of hexachloroplatinic acid (*q.v.*) in a current of chlorine,

$$H_2PtCl_6 = 2HCl + PtCl_4.$$

The salt is reddish in colour. In solution it forms an acid, $H_2PtCl_4(OH)_2$, and does not appear to form platinic ions, $Pt^{++++}$, as might be expected.

*Hexachloroplatinic acid* $H_2PtCl_6$ is present in the solution usually known as platinic chloride. It is obtained when platinum is dissolved in aqua regia,

$$Pt + 2Cl_2 + 2HCl = H_2PtCl_6.$$

It forms reddish-brown needles of composition $H_2PtCl_6.6H_2O$, which are freely soluble in water. When heated, it decomposes first to the dichloride and then to the metal,

$$H_2PtCl_6 = 2HCl + Cl_2 + PtCl_2$$
$$PtCl_2 = Pt + Cl_2.$$

It forms a series of salts known as the chloroplatinates, and these are of particular interest because ammonium and potassium chloroplatinates are practically insoluble in water. It is possible to determine platinum, ammonium or potassium by mixing hexachloroplatinic acid with alcohol and a solution of a potassium or ammonium salt.

$$H_2PtCl_6 + 2NH_4Cl = (NH_4)_2PtCl_6\downarrow + 2HCl.$$
$$[PtCl_6]^{=} + 2NH_4^{+} = (NH_4)_2[PtCl_6].$$

These hexachloroplatinates are yellow crystalline salts. When heated they decompose to a mixture of the metallic halide and platinum,

$$K_2PtCl_6 = 2KCl + Pt + 2Cl_2.$$

Ammonium chloroplatinate leaves platinum only since ammonium chloride is volatile. The chloroplatinates of organic bases behave similarly and their loss of weight when heated affords a useful method of determining their chemical equivalent.

Bromine and iodine form salts analogous to the chloroplatinates.

**1234. Other Platinum Compounds.**—*Platinum sulphate* $Pt(SO_4)_2$ has been described as an orange salt, crystallising with four molecules of water.

No platinum nitrate is known, but there are numerous platinonitrites, $X_2Pt(NO_2)_4$, analogous to the cobaltinitrites (§ 1192).

The *platinocyanides* are of some interest (cf. ferrocyanides, § 576, etc.).

If a platinum salt be warmed with potassium cyanide, potassium platinocyanide is obtained,

$$6KCN + PtCl_4 = K_2Pt(CN)_4 + 4KCl + (CN)_2.$$

The platinocyanides form beautiful crystals, which have a brilliant fluorescent lustre. Barium platinocyanide, which is obtained by the above method, using barium cyanide, forms golden yellow crystals of a peculiar fluorescent lustre. It is used considerably for X-ray screens, as it fluoresces brilliantly under the influence of these rays.

A large number of complex platinum ammines also exist (see § 1237).

## COMPLEX COMPOUNDS OF GROUP VIII.

**1235. Compounds containing Complex Radicals.**—There have been known for many years a number of compounds, the formulæ of which seemed quite at variance with the valency laws as then understood. Such a familiar compound as $K_4Fe(CN)_6$, potassium ferrocyanide, cannot be given any rational structural formula if the valencies of the radicals K, Fe, and CN are given their normal values of 1, 2 or 3, and 1 respectively. The formula may be and was written

$4KCN.Fe(CN)_2$,

as if it were a double salt of potassium cyanide and ferrous cyanide. In fact, its behaviour entirely contradicts this. It does not give the reactions of a cyanide or of a ferrous salt, and the ion $[Fe(CN)_6]^{----}$ is yielded by it. The formula was accordingly written $K_4[Fe(CN)_6]$, and no adequate explanation of the mode of combination of the iron and cyanogen could be given.

Such substances as potassium cobaltinitrite, potassium mercuri-iodide, cuprammonium sulphate, hydrofluosilicic acid presented similar problems, but the most considerable mass of complex compounds was presented by the so-called ammines of metals, notably chromium, cobalt, rhodium, iridium and platinum. These metallic ammines are a very large class, the most recent text-book on the subject cataloguing about a thousand of them.

**1236. The Metallic Ammines.**—These ammines are for the most part fairly difficult compounds to prepare and are somewhat rarely met with in ordinary laboratory practice. The largest class of them are the cobaltammines. These contain tervalent cobalt and are as a rule prepared by oxidising solutions of cobalt salts in excess of ammonia. Their molecules contain one or two atoms of cobalt and a set of other groups, including notably ammonia $NH_3$, water, and various acid radicals. The most peculiar feature about them is that some of these acid radicals are not combined in the same way as in an ordinary salt.

Out of the many hundred cobalt compounds of this nature four may be selected as typical.

(*a*) $Co(NH_3)_6Cl_3$, Hexamminocobaltic chloride.
(*b*) $Co(NH_3)_5Cl_3$, Chloropentamminocobaltic chloride.
(*c*) $Co(NH_3)_4Cl_3$, Dichlorotetramminocobaltic chloride.
(*d*) $Co(NH_3)_3(NO_2)_3$, Trinitritotriamminocobalt.

We encounter on examining these compounds the curious fact that in some cases only a part of the halogen or other acid radical is ionisable. Thus the compound (*a*) hexamminocobaltic chloride precipitates all its halogen as silver chloride when mixed with cold silver nitrate solution, while (*b*) only precipitates two-thirds, and (*c*) one-third. The compound (*d*) does not behave as a salt at all ; it has none of the reactions of a cobalt salt or of a nitrite nor does its solution conduct electricity. It appears that in every case *six* groups are attached to the cobalt atom by co-ordinate linkages, while the remainder are attached by the ordinary ionisable linkage appropriate to salts.

**1237. Constitution of the Ammines**—Werner, who with Jörgensen and some others, has done most to elucidate the constitution of these compounds, wrote the formulæ we have given above as :—

(*a*) $[Co(NH_3)_6]Cl_3$.
(*b*) $[Co(NH_3)_5Cl]Cl_2$.
(*c*) $[Co(NH_3)_4Cl_2]Cl$.
(*d*) $[Co(NH_3)_3(NO_3)_3]$.

denoting thereby the fact that in the first compound all the chlorine is ionisable ; in the second, two-thirds of the chlorine ; in the third, one-third of the chlorine ; while in the last no ions at all are formed.

The platinum ammines provide an even more striking example. The following series of compounds is known, of which the formulæ are given on page 801.

Werner's theory provided an excellent guide to the behaviour of these and

| Formula. | Formula written on Werner's System. | Valency of Complex. | Proportion of Chlorine Ionised. |
|---|---|---|---|
| $Pt(NH_3)_6Cl_4$ | $[Pt(NH_3)_6]Cl_4$ | + 4 | 100 per cent. |
| $Pt(NH_3)_5Cl_4$ | $[Pt(NH_3)_5Cl]Cl_3$ | + 3 | 75 ,, |
| $Pt(NH_3)_4Cl_4$ | $[Pt(NH_3)_4Cl_2]Cl_2$ | + 2 | 50 ,, |
| $Pt(NH_3)_3Cl_4$ | $[Pt(NH_3)_3Cl_3]Cl$ | + 1 | 25 ,, |
| $Pt(NH_3)_2Cl_4$ | $[Pt(NH_3)_2Cl_4]$ | 0 | 0 ,, |
| $Pt(NH_3)Cl_5K$ | $[Pt(NH_3)Cl_5]K$ | − 1 | 0, one $K^+$ ion |
| $PtCl_6K_2$ | $[PtCl_6]K_2$ | − 2 | 0, two $K^+$ ions |

similar compounds. His theory of their behaviour may be summed up as follows :—

(*a*) Certain atoms tend to attach to themselves a definite number, usually four or six, of other atoms or groups which might be whole molecules or radicals. The number is called the *co-ordination number* of the atom.

(*b*) The complex so formed was not a salt, *i.e.*, it did not ionise, but it might combine with other radicals to form a salt-like compound.

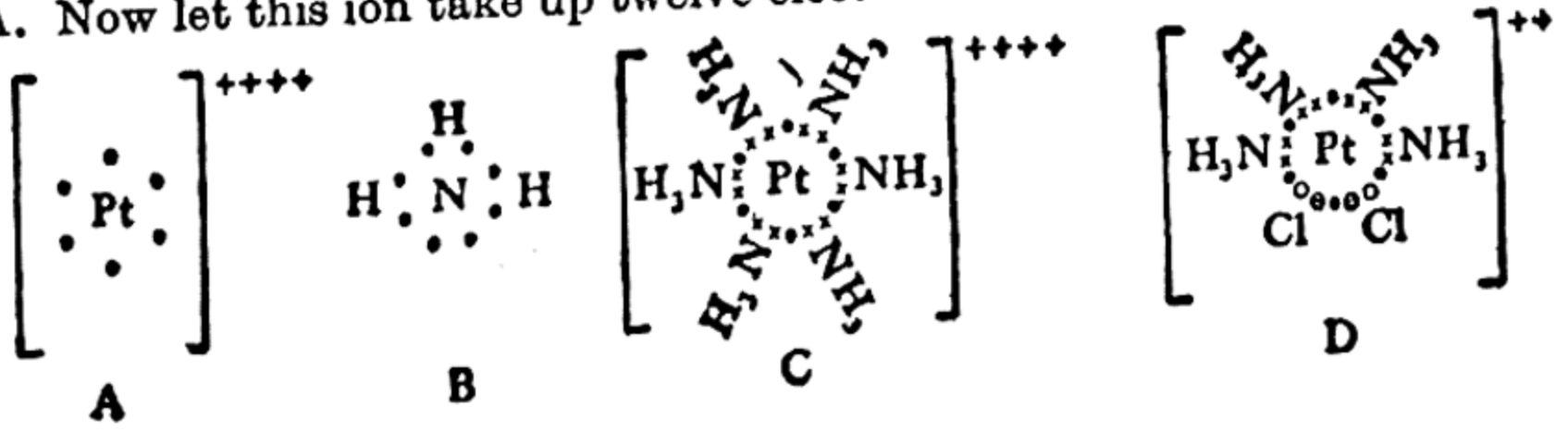
(*c*) When a univalent radical such as chlorine $Cl^-$ displaces a complete molecule ($NH_3$) or ($H_2O$) from the complex its positive valency drops by one unit.

**1238. Electronic Constitution of the Ammines.**.—Werner was unable to explain why these peculiar conditions applied to these compounds, and it was not until Sidgwick connected his theories with Bohr's electronic theory of valency that the matter was cleared up.

Let us consider the case of the platinum ammines cited above. The platinum atom has two incomplete electronic groups and we may represent it diagrammatically thus :—

| | Electrons in Orbits of | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 quantum. | 2 quanta. | 3 quanta. | 4 quanta. | 5 quanta. | | 6 quanta. |
| | | | | | $5_1$ and $5_2$ | $5_3$ | |
| Platinum atom . | 2 | 8 | 18 | 32 | 8 | 8 | 2 |
| Tetravalent platinum ion . . | 2 | 8 | 18 | 32 | 8 | 6 | 0 |
| 'Stable state' corresponding to inert gas structure . . | 2 | 8 | 18 | 32 | 8 | 10 | 8 |
| | COMPLETED GROUPINGS. | | | | | INCOMPLETE GROUPINGS. | |

We may then represent the platinum ion, omitting completed groups, as at A. Now let this ion take up twelve electrons from ammonia molecules (B)



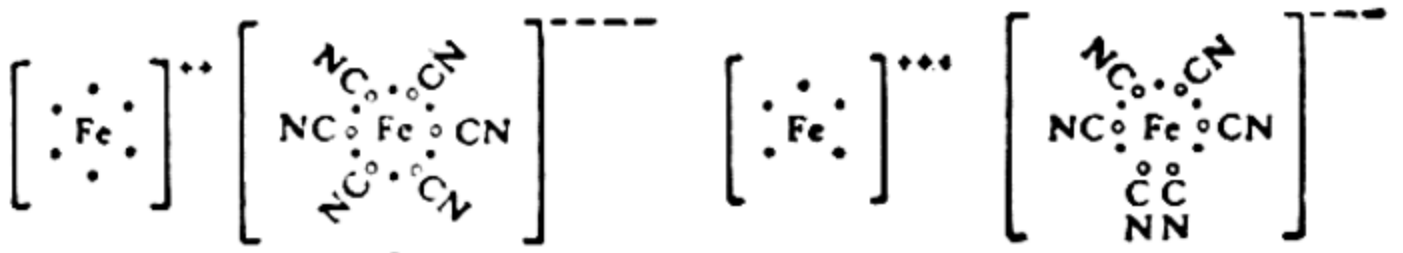
which attach themselves to it by sharing with it their 'lone pair' of electrons. We have then the arrangement shown at C, the electrons derived from ammonia being figured as crosses. The platinum ion has now the stable group of eighteen outer electrons. It has still, however, its original positive charge of four, for the ammonia molecules added to it were electrically neutral.

Consider now the compound $[Pt(NH_3)_4Cl_2]Cl_2$. The six groups surrounding the platinum are four $NH_3$ molecules, each contributing two electrons and two chlorine ions, which can each contribute one electron. We therefore require two more electrons to complete the ring of eighteen, and these are brought from outside. These give the complex an additional negative charge of two units, which reduces its original charge of four positive units to two positive units.

Fig. D shows this state of affairs, the electrons derived from the chlorine atoms being represented by circles, ○, and those taken from outside by barred circles, ⊖.

By the application of similar principles the valency considerations which apply to any of the ammines and to the complex cyanides (§ 576), nitrites (§ 1192) and water compounds (§ 997) may be elucidated.

It is not only to the ammines that the above principles may be applied. Let us consider the case of the ferrocyanides and ferricyanides. A ferrous ion has six electrons (.) in uncompleted groups, and may be represented as at A. It takes up six cyanide groups (CN —) and receives from each its one outer electron (°), (B). In this way its electronic outer layer reaches the figure of 12, which (like 8 and 18) represents a particularly stable grouping of electrons. Its charge was originally + 2($Fe^{++}$), but it has taken on six groups, each with a charge of — 1, and accordingly the charge on the complex is — 4. In the same

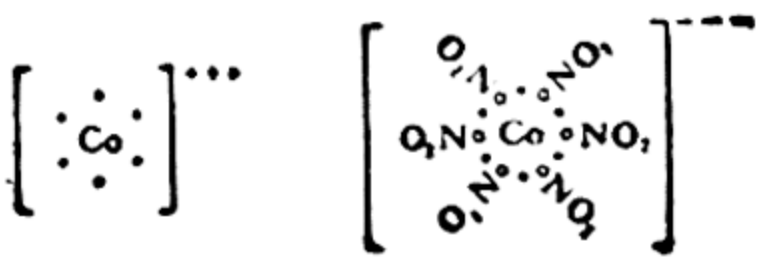



A B

Ferrous ion. Ferrocyanide ion. Ferric ion. Ferricyanide ion.

way a ferric ion has five electrons and a charge of + 3. This takes on six cyanide groups, and its final charge therefore — 3. In this case, however, the stable grouping of twelve electrons is not attained and the ferricyanides are much less stable than the ferrocyanides. It is significant that in the complex cobalt cyanide compounds it is the cobalt*i*cyanides which are stable, while the cobalt*o*cyanides are not. The cobalt atom has one more electron than the iron atom, hence it is the cobalticyanides which have the stable 12-electron ring.

A final example may be taken in potassium cobaltinitrite $K_3Co(NO_2)_6$. The cobalt atom has incomplete outer groups of seven and two electrons and the cobalt*ic* ion from which the salt is ultimately derived has then six electrons in incomplete groups (A). By adding on six nitrite groupings ($NO_2$ —) it




Cobaltic ion $Co^{+++}$. Cobaltinitrite ion. $Co(NO_2)_6^{---}$.

receives six negative electrons (o'), thus making an outer set of twelve and diminishing its charge from + 3 to — 3.

The preparation of most of the metallic ammines is not particularly easy. the student may, however, wish to prepare one of the series, and the following preparation may be quite easily carried out.

*Chloropentamminochromic Chloride.*—Arrange a 1-litre flask, glass-wool filter and beaker as in Fig. 195. Remove the flask and place in it 10 gms. powdered potassium dichromate and 80 gms. granulated zinc. Add a mixture of 60 c.c. fuming hydrochloric acid and 30 c.c. water. A violent reaction ensues and reduction to blue chromous chloride should take place. If not, add more concentrated acid. Then replace the cork and tube, and blow the mixture into a large beaker containing a good excess of ammonia solution. A deep blue solution is formed, and this is transferred to a wash-bottle and a stream of air is passed through it until it becomes crimson. The solution is filtered from

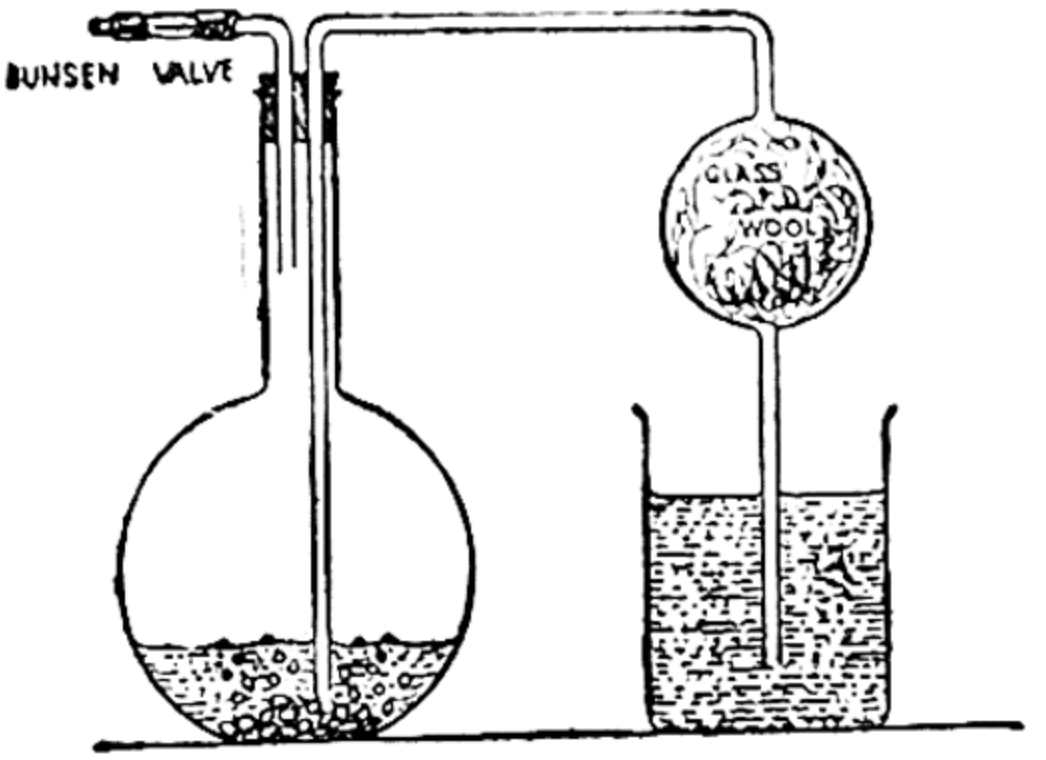



FIG. 195.—Reduction of Chromic Chloride.

chromic hydroxide and a large excess of concentrated hydrochloric acid is added. Deep red crystals of chloropentamminochromic chloride are precipitated and may be filtered off and dried on absorbent paper. The reactions are :—

$$K_2Cr_2O_7 + 8HCl + 3C_2H_5OH = 2KCl + 2CrCl_3 + 3C_2H_4O + 7H_2O$$

$$2CrCl_3 + Zn = 2CrCl_2 + ZnCl_2$$

$$Cr^{++} + 4NH_3 \rightleftharpoons Cr(NH_3)_4{}^{++}$$

$$2Cr(NH_3)_4{}^{++} + 2NH_3 + 2H^+ + O + 3Cl^- = 2[Cr(NH_3)_5Cl]Cl_2 + H_2O.$$

The fact that only a portion of the chlorine is ionised is demonstrated by dissolving the salt in cold water, adding excess of silver nitrate and shaking Silver chloride is precipitated. The solution is filtered and, when boiled, loses its red colour, and precipitates a further portion of silver chloride, thus demonstrating that a part of the chlorine was an integral part of the red complex ion.

# CHAPTER XXV

## THE INERT GASES

**1239. Historical.**—None of the members of this remarkable group of elements, which comprises *helium*, *neon*, *argon*, *krypton*, *xenon*, *radon* (or *niton*), was discovered until 1894, despite the fact that argon forms nearly 1 per cent. of atmospheric air. Nearly a hundred and fifty years ago (1785) Cavendish subjected a mixture of oxygen and air to the continued action of electric sparks and then absorbed the excess of oxygen and the oxides of nitrogen by means of 'liver of sulphur,' potassium pentasulphide. He found in this way that all the nitrogen was converted into oxides and that all the gas was absorbed except a very small proportion and wrote, "If there is any part of the phlogisticated air[1] of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than 1/120 part of the whole."

It is very remarkable that no one attempted to find out whether atmospheric nitrogen was a pure substance until a hundred and nine years had elapsed.

In 1894, Rayleigh determined the density of nitrogen with great accuracy. His experimental error was estimated to be about 0·01 per cent., but the difference between his results for the density of nitrogen made from the air and nitrogen chemically prepared from its oxides, ammonia, etc., amounted to 0·47 per cent. By a repetition of Cavendish's experiment a residue of gas with a spectrum differing from that of nitrogen was obtained; and, finally, by removing the oxygen and nitrogen and carbon dioxide from dry air by absorption with red-hot copper and magnesium, a new gas was isolated.

$$2Cu + O_2 = 2CuO$$
$$3Mg + N_2 = Mg_3N_2.$$

The new gas was shown to have an atomic weight of 40, and after some discussion was relegated, together with the other inert gases discovered soon after, to a separate group in the Periodic table, Group 0. This group was placed intermediately between Group VII., the intensely electronegative halogens, and Group VIII., the intensely electropositive alkali metals.

[1] Nitrogen.

**1240. Preparation of the Inert Gases.**—Helium, as mentioned below, can be obtained from certain minerals, from mineral springs and from natural gas, niton is obtained from certain radioactive elements, while the other gases are only obtainable from the air.

The inert gases may be separated from air by chemical absorption of all other constituents, or may be obtained from it by fractional distillation of liquid air. The latter method is employed commercially on a large scale.

**1241. Preparation of the Inert Gases by Chemical Methods.**—(1) Cavendish's method has been perfected by Rayleigh and

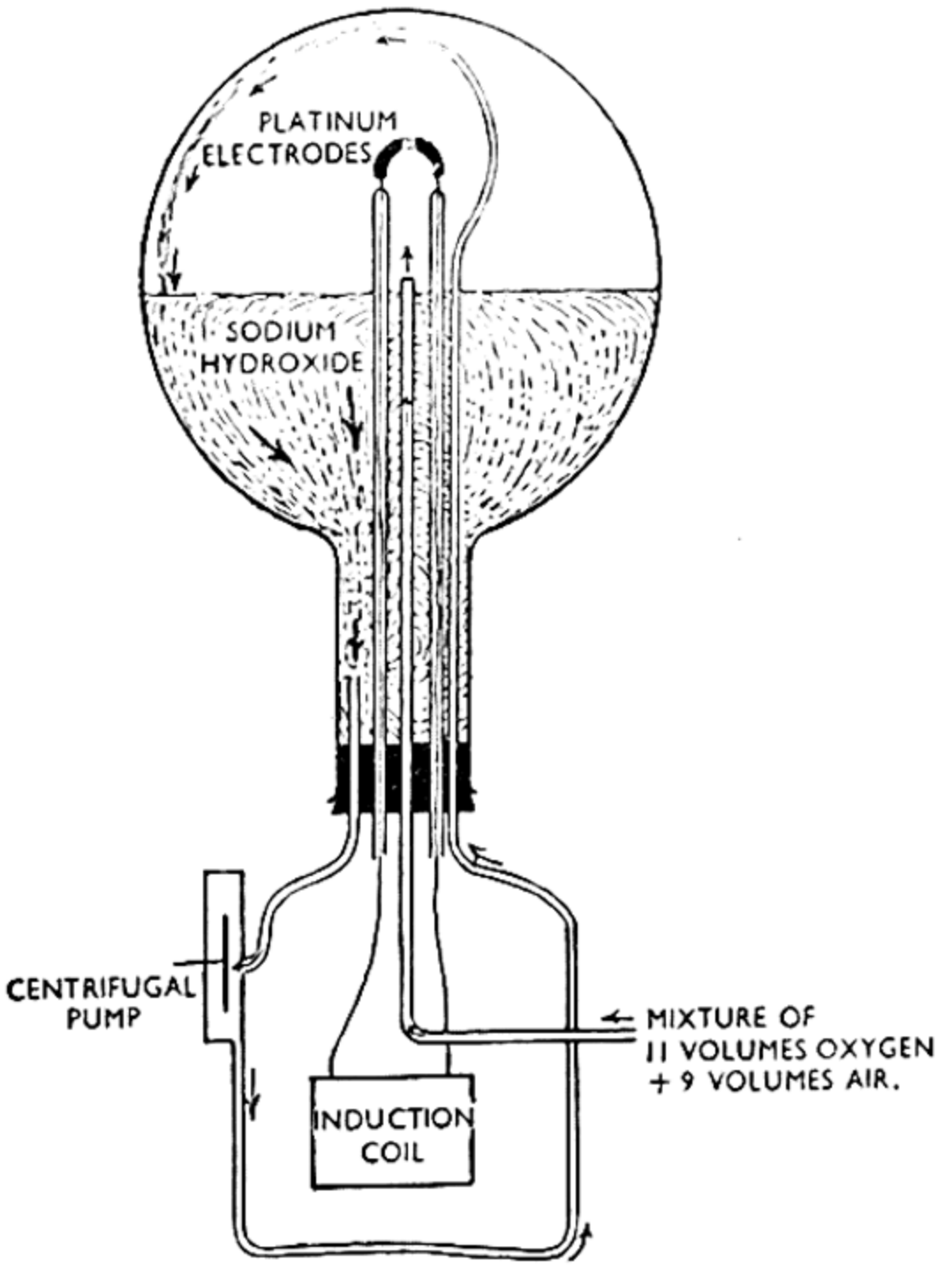



FIG. 196.—Extraction of Inert Gases from Air.

Ramsay. A flask, fitted as in Fig. 196, with arrangements for circulating caustic soda solution, has in it a pair of heavy platinum electrodes between which passes a discharge from an induction coil of about 2,000 volts. The flask contains a mixture of oxygen and air (11 vols. : 9 vols.) and this mixture is supplied through a tube as fast as it is used up. The oxygen and nitrogen react to form oxides of nitrogen and these are absorbed by the caustic soda.

$$N_2 + O_2 = 2NO$$
$$2NO + O_2 = 2NO_2$$
$$2NO_2 + 2NaOH = NaNO_2 + NaNO_3 + H_2O$$

Argon and the other rare gases accumulate in the flask together with a little oxygen, which is removed by absorption with pyrogallol. The other rare gases can only be separated from argon by fractionation of the liquefied material.

(2) Ramsay used magnesium to absorb nitrogen, but the reaction is very slow. Calcium or barium is better. The best chemical method appears to be absorption by calcium carbide. Air is circulated through an iron retort containing calcium carbide mixed with 10 per cent. of the chloride, and maintained at 800° C.

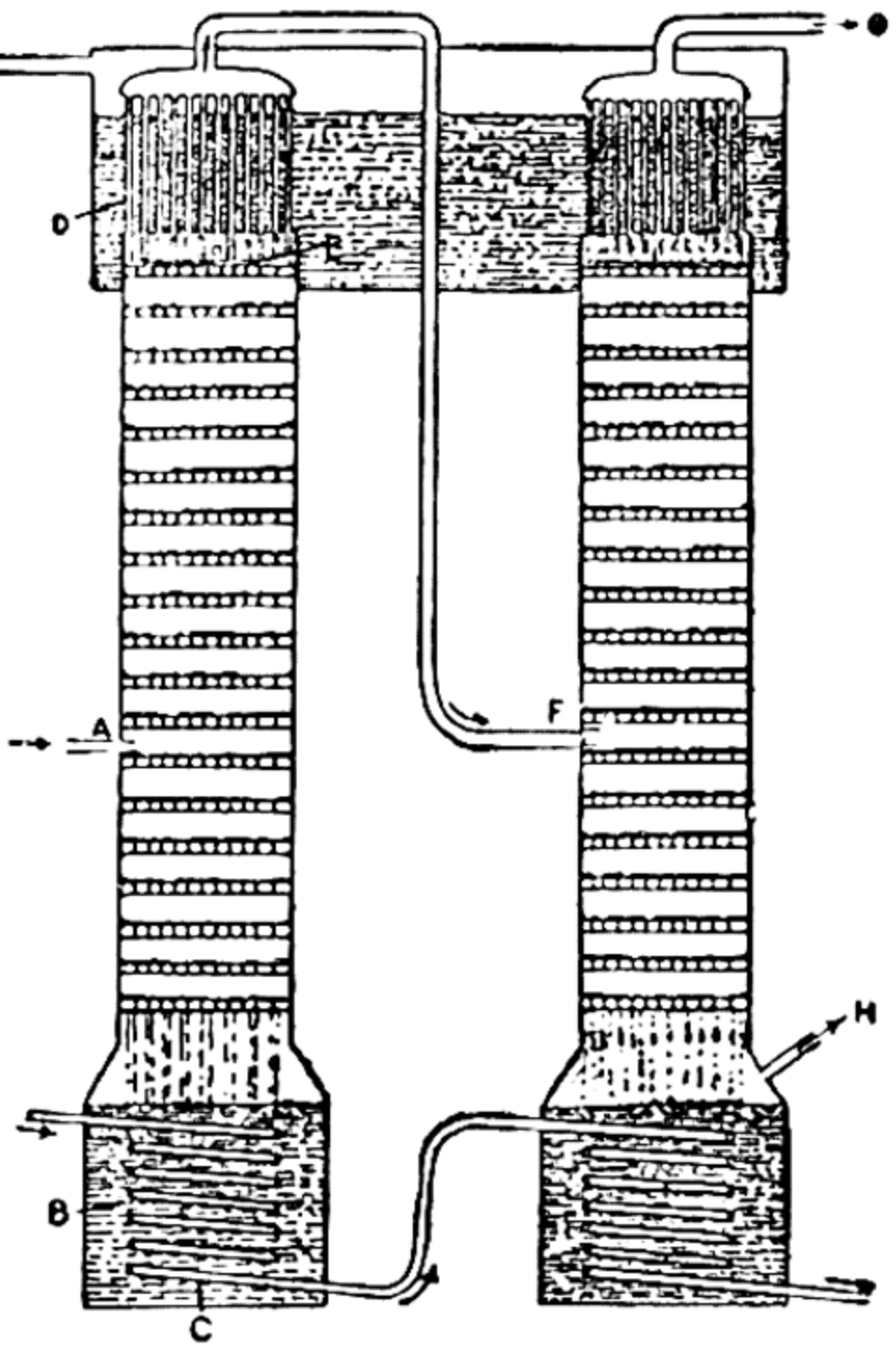


FIG. 197.—Linde Argon Column.

The reactions :—

(1) $CaC_2 + N_2 = CaCN_2 + C.$

(2) $C + O_2 = CO_2.$

result in the oxygen and nitrogen being absorbed. Some carbon monoxide is produced and is removed by including in the air circulation a tube containing red hot copper oxide and a potash absorption apparatus,

$$CO + CuO = Cu + CO_2$$

$$CO_2 + 2KOH = K_2CO_3 + H_2O.$$

Water vapour, which might affect the carbide, is removed by concentrated sulphuric acid and potash.

Eleven litres of argon were obtained by this method in two days.

**1242. Inert Gases from Liquid Air.**—The inert gases are produced commercially by the fractionation of liquid air.

Helium and neon boil at lower temperatures than nitrogen, the boiling point of the first being 73° C. below and the second 43° C. below the boiling point of nitrogen. They accordingly resist liquefaction in the ordinary nitrogen separation process and there collects above the liquid ( (N) Fig. 127) in the liquefying column, a mixture of nitrogen, neon and helium. This mixture is led to a spiral tube placed in the stream of evaporating liquid nitrogen (near F) and there the greater part of the nitrogen is condensed as liquid. A mixture of helium and neon, with some 50 per cent. of nitrogen, passes on and is purified by chemical means (absorption of nitrogen

by calcium carbide, etc.). The resulting gas contains about three vols. of neon to one of helium.

Further separation is difficult and requires the use of liquid hydrogen.

Argon boils at a temperature 3° C. below the boiling point of oxygen, and this small temperature difference makes its isolation difficult. The Linde argon column (Fig. 197) has been used for its separation.

The liquid oxygen formed in the air liquefaction process contains most of the argon of the air and this material is run into the base of the two columns at B. Compressed air, passed through the coils C, evaporates some of the liquid, and the gas evaporated from the liquid is richer in argon than the original liquid. This gas travels up through a rectifying column and is scrubbed by liquid oxygen condensed out at the top of the column D by a bath of boiling nitrogen E (– 195° C.). This cold oxygen, running back, condenses out oxygen from the rising gas and itself has argon evaporated from it. The enriched argon-oxygen mixture undergoes the same process in a second column and the remaining proportion of oxygen (and nitrogen) is then removed by chemical treatment.

## HELIUM He, 4·003

**1243. Historical.**—In 1868 a new spectrum was observed in the chromosphere, or atmosphere of glowing gas, which surrounds the sun. The name helium (Gr. ἥλιος, *helios*, the sun) was given to the element, then unknown on earth, which gave rise to it. A uranium mineral, called cléveite, was examined in 1889 by Hillebrand, and he obtained from it what he concluded to be nitrogen. Though the gas gave spectral lines not attributable to nitrogen, the fact that the gas actually contained nitrogen led him to believe that the gas actually was nitrogen. Ramsay suspected, after his discovery of argon, that this gas obtained by Hillebrand might really be argon. By heating cléveite with dilute acid he obtained a gas, the spectrum of which was found to be identical with the 'helium,' hitherto only known in the sun's chromosphere.

**1244. Preparation.**—Helium is a degradation product of many radioactive elements (Chapter XXVI.) and is contained in all radioactive minerals, *i.e.*, uranium and thorium minerals. It is not combined with these, but adsorbed, the atoms being driven into the solid mineral by the violence of the radioactive changes.

When these minerals, best cléveite or monazite sand (§ 667), are strongly heated *in vacuo* the gas is given off.

Helium is found in many gases evolved from hot springs, etc.,

which may contain up to 5 per cent. of the gas. It is obtained in enormous quantities from the *natural gas* (§ 537) now so greatly used in the U.S.A. as a source of heating and power.

It is estimated that more than a million cubic feet of helium run to waste yearly in natural gas. A typical natural gas may contain: Helium 0·9 per cent., carbon dioxide 0·25 per cent., oxygen 0·5 per cent., hydrocarbons (methane, ethane, etc.) 67 per cent., nitrogen 31 per cent. Carbon dioxide is removed by washing with lime-water, and the gas is then liquefied and rectified in much the same way as that in which nitrogen is separated from air. The helium (B.P., – 268·7° C.) passes on together with a little nitrogen, while the hydrocarbons are evaporated and burnt for power, etc. The helium contains *c.* 5 per cent. of nitrogen and if used for filling air-ships is not further purified. The residual nitrogen may be removed chemically.

Helium can also be prepared by the liquefaction process described in § 1242, but its separation from neon is difficult.

**1245. Properties.**—Helium is a colourless gas without taste or smell. It has a density of 2·00 (0 = 16) and is therefore the second lightest gas.

Helium is monatomic, as shown by the ratio of its specific heats $C_p/C_v = 1{\cdot}652$. Helium is liquefied only with the greatest difficulty, the boiling point of liquid helium being 4·22° absolute, – 269·01° C. The ordinary air-liquefaction process cannot be used until the gas has been cooled to 15° A. by means of boiling liquid hydrogen. The density of liquid helium is 0·146, and it is therefore lighter than any other solid or liquid except liquid hydrogen (density 0·07).

The evaporation of liquid helium gives one of the most efficient methods of attaining low temperatures. When further cooled to 2·19° A., liquid helium changes into a second form known as helium II. This liquid has extraordinary properties which find no analogy elsewhere. It is an almost perfect conductor of heat, some 300 times superior to copper, and its viscosity is minute, between a ten thousandth and a millionth of that of water.

Helium cannot be solidified by cooling alone, but under a pressure of *c.* 25 atm. it solidifies to a substance melting at about 1° A.

Helium is slightly soluble in water. The spectrum has been very fully investigated (p. 173). It has a conspicuous green line, by which the gas may be recognised.

Helium is generally supposed, in common with the other inert gases, to form no compounds.

Helium has been used in the U.S.A. for the filling of dirigibles. It serves the purpose admirably. It is non-inflammable, and while it is not so light as hydrogen it has a further advantage that it escapes

through the bag fabrics less easily. Europe possesses no adequate source of the gas, and the expense of transporting it across the Atlantic in heavy iron cylinders would be prohibitive.

### NEON Ne, 20·183

**1246. Discovery and Preparation.**—The gas neon was discovered by Ramsay and Travers in 1898. A gap appeared to exist in the Periodic table between helium and argon, and they liquefied 18 litres of argon and allowed it to evaporate, collecting the gas in fractions. In the first fraction they found a gas with a new spectrum and by fractionating it again obtained a gas with a density of 10·1.

Neon is now made in quantity for the filling of neon tubes by the methods described in § 1242.

**1247. Properties.**—Neon is colourless, tasteless and odourless. Its density is 10·1 and its atomic weight 20·18. It contains three isotopes of atomic weights, 20, 21 and 22. Neon can be liquefied at the temperature of boiling hydrogen. Its boiling point is − 246° C. and solid neon melts at − 250° C.

The spectrum of neon has lines in the orange and red.

Neon finds its chief use in the construction of neon-lamps. These are used enormously as advertising signs. The lamp consists of glass tubes, 10 to 20 feet long, furnished with electrodes at either end, and containing neon at a much reduced pressure (2 mm. Hg.). A voltage of 1000 volts is applied to these and a fine reddish-orange glow is produced. A mixture of argon and a little mercury vapour gives a fine blue, and a mixture of neon and helium a gold[illegible]ur. The use of coloured glass tubes gives other variations.

These inert gas discharge lamps can now be made to operate off the ordinary electric mains. Most of them contain mercury vapour and an inert gas and give out most of their energy as ultra-violet radiation. The tubes are coated internally with fluorescent chemicals such as magnesium tungstate, or cadmium borate, which convert a part of the ultra-violet light into visible light. These tubes are widely used for the purpose of artificial illumination, because the best of them are as much as six times more efficient than the standard filament lamps in converting electrical energy into light.

### ARGON A, 39·944

**1248. Preparation.**—The preparation from the air of argon (containing traces of krypton and xenon) is described on p. 801. Argon is also found in the gases from certain mineral springs.

Pure argon is prepared by fractional distillation of liquefied 'atmospheric' argon at the temperature of liquid air. It boils at − 186·1° C., and so helium and neon boil off in the first fractions

evaporated, while krypton and xenon remain till the last.

**1249. Properties.**—Argon is colourless and without taste or smell. Its density is 19·95 and its atomic weight 39·94. The fact that argon has a higher atomic weight than potassium, though it precedes it in the Periodic table, was not explained for some time. It is realised now that the atomic weight is not the true determining factor in the Periodic table, the important fact being that argon has a smaller nuclear charge than potassium though it has a heavier nucleus. Two isotopes of argon exist of atomic weights 40 and 36.

Argon is more soluble in water than either nitrogen or oxygen. It is liquefied at the temperature of liquid air, and the liquid boils at − 186·1 and freezes at − 187·9° C.

Argon is believed to form no compounds, though there has been some question of the existence of a hydrate.

**1250. Uses.**—Argon has been used for filling metal-filament electric lamps. Its chemical inertness fits it well for this purpose, and it can now be manufactured sufficiently cheaply from air.

### KRYPTON Kr, 83·7, and XENON Xe, 131·3

**1251. Discovery and Preparation.**—Krypton was discovered by Ramsay and Travers in the final residues obtained when some 30 litres of liquid air were allowed to evaporate. The spectra of two new gases named *krypton* (κρυπτόν, hidden) and *xenon* (ξενόν, the stranger) were detected and their atomic weights ascertained as roughly 85 and 130.

These gases occur only in the smallest proportion in air, krypton forming some 1/20,000,000 part and xenon the 1/170,000,000 part by volume. They are obtained by passing dry carbon dioxide free air through a spiral tube packed with glass wool, and immersed in boiling liquid air. The krypton and xenon condense as liquids or solids. They may be separated from each other by fractionating the solids, krypton being much more volatile.

**1252. Properties.**—The density of krypton is 41·8 and its atomic weight is 83·7. It is composed of numerous isotopes of atomic weights 78 to 86. Krypton is liquefied without difficulty and boils at − 151° C. The solid melts at − 157° C.

Xenon has a density of 65·35 and an atomic weight of 131·3. Nine isotopes of atomic weights of 124 to 136 are known. Xenon is liquefied more easily than krypton, boiling at − 109° C. The solid melts at about − 112° C.

Both krypton and xenon give characteristic spectra by which they may be detected.

### RADON Rn (Em), 222

**1253. Preparation and Properties.**—Radium, thorium and actinium all give off radioactive gases during their radioactive decomposition (p. 817). These three gases are known as the emanations of these metals, or as radon, thoron, and actinon, respectively. They are all three isotopes of the same element, which is known as *niton*. Thoron and actinon are very shortlived and of little practical

importance, but radon is not too transient to be handled. Radium decomposes very slowly, one half disappearing in 1,580 years. One half of any quantity of radon, however, disappears in 3·8 days, and consequently only the minutest quantities can be obtained from the small quantities of radium available.

From a gram of radium about 4 c.mm. a day are produced (about ·004 mg.).

To obtain radon a radium salt is dissolved in water. Radon is produced, and also oxygen and hydrogen, as a result of the energy of decomposition of the radium. From this gas radon may be condensed in a spiral tube cooled by liquid air.

The largest quantity of pure radon yet obtained is about $\frac{1}{1400}$ mgm., yet the density of this minute amount has been determined by direct weighing on a micro-balance sensitive to ·000002 mg., and its density has been found to be 111·5, which would give an atomic weight 223. From the theory of radioactivity the atomic weight should be that of radium less that of helium, 225·9 − 4·0 = 221·9.

Its spectrum has been obtained. Radon boils at about − 62° C. and freezes at − 71° C. The liquid is strongly luminous with a light varying from blue to orange-red. The gas has the properties associated with intensely radioactive substances, causing the decomposition of water and many other compounds.

# CHAPTER XXVI

## THE RADIOACTIVE AND TRANSITORY ELEMENTS

**1254. Historical.**—The phenomenon known by the name of radioactivity is exhibited by certain elements of high atomic weight and by their compounds. Of these elements uranium and thorium have been known for many years, but since they exhibit but feeble radioactive properties these remained undetected until the close of the nineteenth century (1896), when Becquerel discovered that uranium compounds emitted rays which affected a photographic plate. A systematic examination of uranium and thorium minerals soon led to the discovery of numerous radioelements, present in extremely

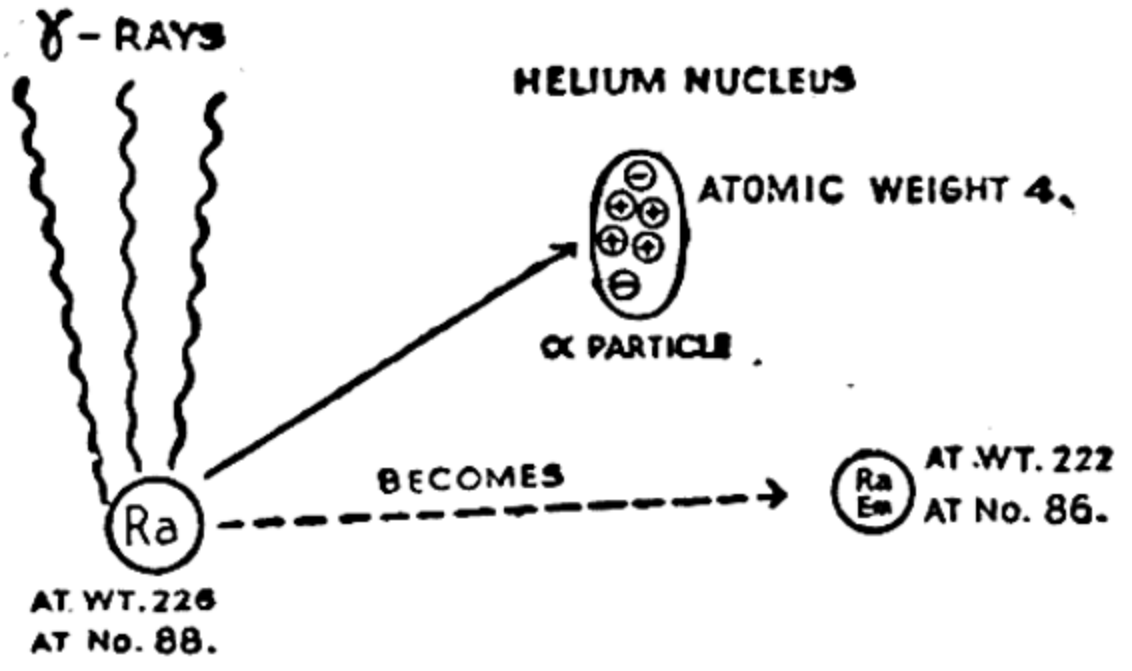



FIG. 198.—Decomposition of an atom of radium.

small quantity but manifesting very great activity. Notable amongst these was the element radium, separated from pitchblende by Mme. Curie. This element, of atomic weight 226 and of chemical properties analogous to barium, showed a most remarkable series of phenomena. Some thirty or more elements[1] with radioactive properties are now known.

The two characteristic properties of radioelements are their emission of radiations of peculiar character and their simultaneous transformation into other elements.

**1255. Radiations.**—All radioelements emit radiations which affect a photographic plate and which have the power of ionising the air and therefore of discharging an electroscope. They may also cause certain substances (*e.g.*, barium platinocyanide and zinc sulphide) to

[1] Including isotopes.

phosphoresce. It was early noted that these rays were complex, and Rutherford and various other workers have since established that they are of three kinds.

(1) *Alpha-rays.*—These consist of a stream of particles of matter travelling at high speeds—about a twentieth of the velocity of light, on the average. The particles are helium nuclei, *i.e.*, helium atoms lacking the two electrons which are outside the nucleus. They are comparatively heavy, having four times the weight of a hydrogen atom, and since they have an enormous velocity they have considerable kinetic energy and produce large effects where they strike. An idea of their energy may be gained from the fact that if a rifle bullet could be fired with the velocity of an $\alpha$-particle it would do as much damage to the thing it hit as would a collision with 125 express trains travelling at seventy miles an hour. The $\alpha$-particles do not travel far, for collisions with the molecules of the air pull them up within a distance of 3 to 11 cm. (at N.T.P.).

(2) *Beta-rays.*—These consist of electrons projected with enormous velocities—up to 99 per cent. of that of light—and in their properties resemble 'cathode rays.'

(3) *Gamma-rays.*—These resemble X-rays and light in that they are electromagnetic vibrations, but differ from them in that they are of exceedingly high frequency and show great powers of penetration through matter.

Rays of all three types are never emitted by any one element in its change into another element.

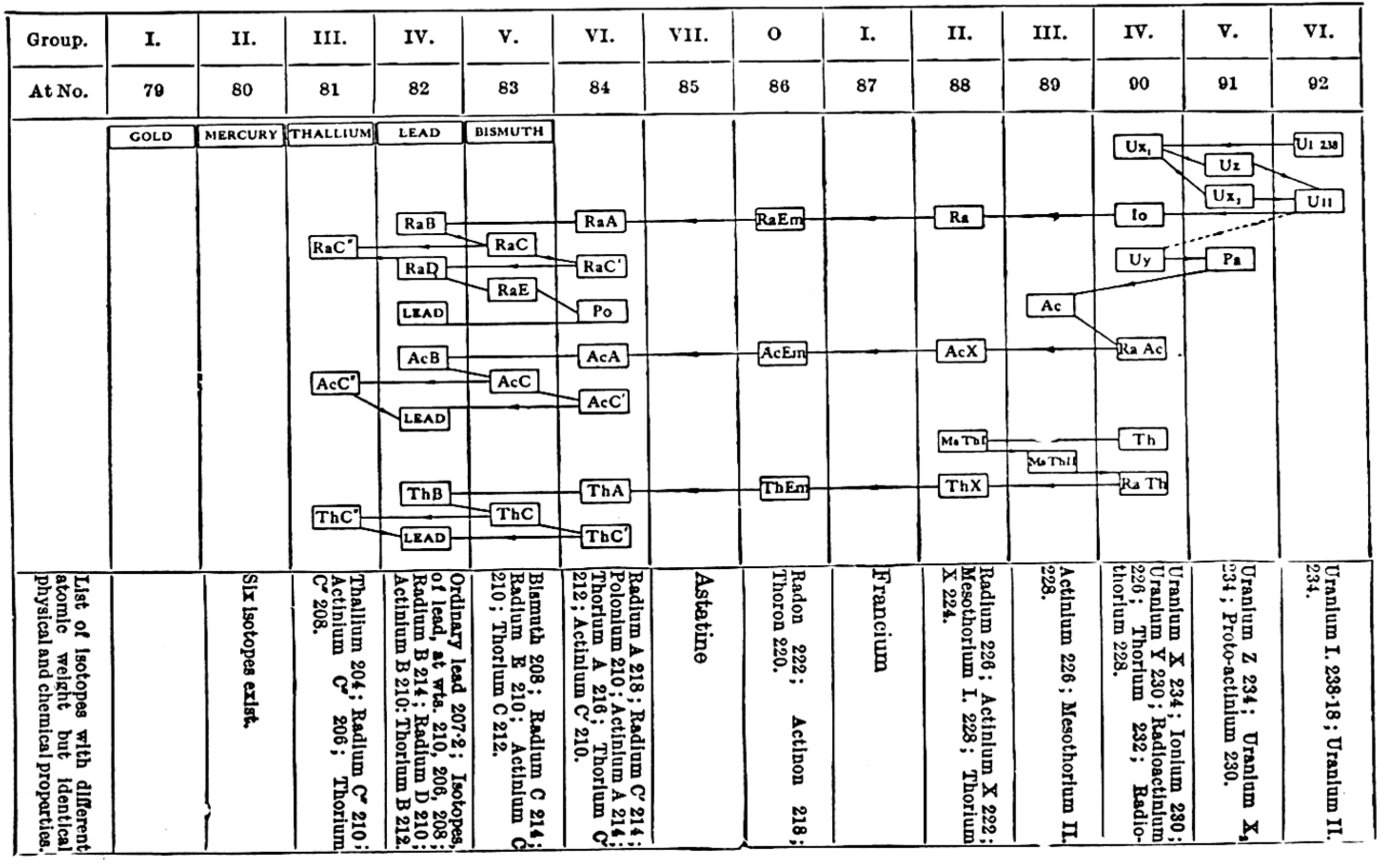
**1256. Radioactive Transformations.**—The most striking fact about radioelements is, however, their transformation into other elements, It has been shown that the emission of rays is always accompanied by such a change. The emission of an $\alpha$-particle changes an atom of an element into an atom of the element with atomic weight four less than the original, and atomic number two less. The emission of a $\beta$-particle transforms the atom into that of an element of the same atomic weight but of atomic number one greater.[1] The investigation of these changes has been a very difficult task, but the following facts are now certain.

(1) Uranium and thorium are the original parent elements, *i.e.*, they are themselves being transformed into other elements, but are not being formed. The period necessary for half of any mass of these elements to change into other elements approximates to $10^9$ to $10^{10}$ years, so that they may well have been formed when the solar system was under conditions of temperature and pressure which allowed of the formation of elements, and may have been decomposing ever since.

[1] See § 141.

FIG. 199.—Periodic Table.

End of Period VI. and beginning of Period VII. showing Radioactive changes.



(2) The products of the disintegration of uranium and thorium atoms themselves disintegrate. By emitting α-particles their atomic weights and atomic numbers are decreased; by emitting β-particles their atomic weights are unchanged, while their atomic numbers increase. The α-particle changes predominate and consequently the elements as a series decrease in atomic weight and atomic number until ultimately they form lead (atomic weight 206–208). Lead is not radioactive and the process goes no further.

The progress of the disintegrations of the elements lighter than uranium is shown in the diagram of Fig. 199.

**1257. Radioactive Isotopes.**—It will be seen from this diagram that there are some forty elements which decompose in this way. These occupy only ten places in the Periodic table. It was supposed at the time when radioactivity was first investigated that every element had its own distinctive set of properties, atomic weight, and position in the Periodic table. Soddy was led by his researches into the properties of these new elements to suppose that certain elements which differed in atomic weight or radioactive properties (range or type of ray or both) had identical chemical and physical properties (in so far as these did not depend directly on atomic weight), and so occupied the same place in the Periodic table. These elements he termed *isotopes* (§ 148). To take an actual example, the element ionium has a much more intense radioactivity than thorium. Yet these two elements are so alike in all other respects that if they are mixed no chemical process, no fractional crystallisation, no known process of separation will separate them, despite the fact that the slightest separation could be detected by the change in radioactivity of the portions.

The radioelements, then, include only ten sets of chemical and physical properties as we ordinarily use the term. These sets of properties are those of the elements given below.

*Elements*

At. No.

81. *Thallium* (§§ 503–4).
82. *Lead* (§ 625 ff).
83. *Bismuth* (§§ 827–841).
84. *Polonium.*—This element was unknown until Mme. Curie isolated it from pitchblende. Its properties are hardly known owing to the minute amounts available, but they appear to resemble but are not identical with those of tellurium, its analogue.
85. *Astatine* (p. 734).

86. *Emanation.*—There are three isotopes of this inert gas, the properties of which are described in § 1253. The isotopes differ in atomic weight and also in their period of decay and consequent activity.
87. *Francium* (p. 293).
88. *Radium.*—This element has properties generally resembling those of barium, and was discovered by Mme. Curie as a result of her investigations of radioactivity. Its properties are discussed in § 1265.
89. *Actinium.*—This element, also new, resembles lanthanum and the elements of Group III. A.
90. *Thorium* is discussed in §§ 667–670.
91. *Protoactinium.*—This element is an analogue of tantalum and resembles it in some properties. It is, however, more basic in character.
92. *Uranium* is discussed in §§ 1015–1027.
93. *Neptunium*
94. *Plutonium*
95. *Americium*
96. *Curium*

} See §§ 1272–1277.

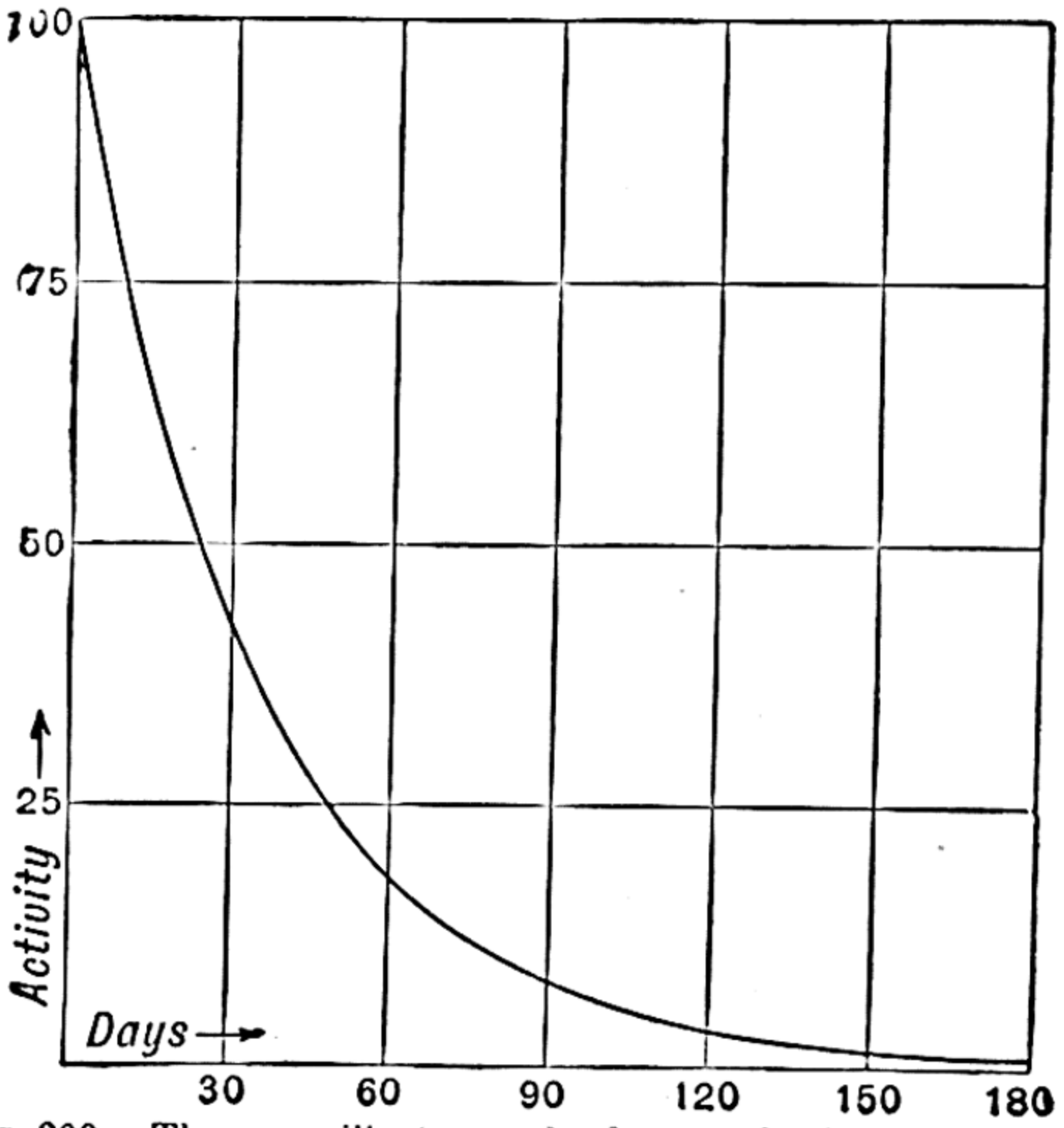



**Fig. 200.**—The curve illustrates the decrease in the activity of a preparation of uranium X. It will be seen that one-half of the element present at any time disappears in the course of 24·6 days.

**1258. Rate of Disappearance of Radioelements.**—The quantity of a radioelement decaying in unit time is directly proportional to the quantity present; *i.e.*, in unit time a certain definite fraction characteristic of the element decays. It follows then that it is impossible to state the period which will be required for the complete decay of a radioelement, for theoretically this is infinite, but it is possible to find the period which will elapse while half of any quantity of the element decays. Fig. 200 shows the curve of decay of a radioelement with the lapse of time. The half-decay period of the radioelement of which the decay curve is drawn in Fig. 200 is 24.6 days.

**1259. Determination of Period of Transformation.**—In the case of elements which decay in a few hours, days or months, the intensity of the radiation may be measured at intervals, the radiation of the products being distinguished from that of the substance decaying by the range of the $\alpha$-particles in air, etc. In some cases the products can be removed. The period of transformation of such elements as uranium, of which an immeasurably small fraction decays even in a life-time, is obtained by Geiger and Nuttall's rule, given below, as also is the period of elements which decay very quickly. If we call the transformation constant [1] of the element $\lambda$ and the range[2] of the $\alpha$-particle in air R, then $\log \lambda = A + B \log R$, where A and B are constants. A has a slightly different value for each family of radioelements, but B has the same value for all (53·9).

The period of transformation of these elements varies enormously, the longest, $1{\cdot}3 \times 10^{10}$ years (thorium), being about $10^{27}$ times the shortest, which is $10^{-6}$ secs. (radium C′). Below is given a list of the radioelements and their periods of transformation :—

| Uranium Series. | | Actinium Series. | | Thorium Series. | |
|---|---|---|---|---|---|
| Uranium I. | $4{\cdot}5 \times 10^9$ y. | Protoactinium | $1{\cdot}2 \times 10^4$ y. | Thorium | $1{\cdot}5 \times 10^{10}$ y. |
| Uranium $X_1$ | 24 d. | Actinium | 20 y. | Mesothorium I. | 6·7 y. |
| Uranium $X_2$ | 1·15 m. | Radioactinium | 19 d. | Mesothorium II. | 6·2 h. |
| Uranium II. | $2 \times 10^6$ y. | Actinium X | 11·5 d. | Radiothorium | 1·9 y. |
| Uranium Y | 25 h. | Actinium emanation | 3·92 s. | Thorium X | 3·64 d. |
| Ionium | $10^5$ y. | Actinium A | 0·002 s. | Thorium emanation | 5·4 s. |
| Radium | 1600 y. | Actinium B | 36·1 m. | Thorium A | 0·14 s. |
| Radium emanation | 3·8 d. | Actinium C | 2·15 m. | Thorium B | 10·6 h. |
| Radium A | 3·0 m. | Actinum C′ | 0·005 s. | Thorium C | 60·8 m. |
| Radium B | 26·8 m. | Actinium C″ | 4·76 | Thorium C′ | $10^{-11}$ s. |
| Radium C | 19·5 m. | Lead. | | Thorium C″ | 3·2 m. |
| Radium C′ | $10^{-4}$ s. | | | Lead. | |
| Radium C″ | 1·32 m. | | | | |
| Radium D | 16 y. | | | | |
| Radium E | 5·0 d. | | | | |
| Polonium | 136 d. | | | | |
| Lead. | | | | | |

1 The fraction of the element transformed in unit period of time.

2 The 'range' of the $\alpha$-particle is the distance it travels before it is stopped by collisions with the molecules of air at N.T.P., and is a definite and easily determined quantity.

**1260. Special Properties of Radioactive Matter.**—*Heating Effects.*—Radioactive matter is continually emitting energy in the form of the kinetic energy of its $\alpha$- and $\beta$-particles and the radiant energy of the $\gamma$-rays. Much of this energy appears as heat, partly due to the recoil of the atom emitting the particle and partly to the collisions of the $\alpha$-particles with matter. Radium produces 134·7 calories per gram per hour, heat enough to keep it perceptibly warm. This amounts to a relatively enormous sum of energy when the time for which it continues (1,580 years for half-decay) is considered. Actually, 1 gm. of radium emanation emits $3{\cdot}7 \times 10^9$ gm-calories during its life. One gram of hydrogen burning to water emits only $3{\cdot}4 \times 10^4$ calories. Evidently enormous stores of energy are locked within the atom, and some small part of these are released during atomic disintegration.

*Electrical Effects.*—The emission of charged particles, $\alpha$- and $\beta$-rays, charges the surrounding air molecules with electricity. This charge is due, not so much to the actual charge on these particles but to their tearing electrons from the atoms in their paths. This fact enables us to track the course of an $\alpha$-particle. The particle leaves behind it a trail of ions, and on these water will condense from a saturated vapour. These trails can be photographed and Plate XIX. shows some of the results obtained. The small size and great energy velocity of the $\alpha$-particle enables it to penetrate other atoms and even to enter and break up their nuclei. Plate XIX. shows the track of an $\alpha$-particle which has collided with a nitrogen atom, detaching from it a proton. The faint straight branch is the track of the former. The $\alpha$-particle is apparently captured by the nucleus, forming an isotope of oxygen.

The intense ionisation caused by $\alpha$-particles allows of their being counted, for a single $\alpha$-particle produces enough ions to cause a gas to conduct sufficiently well to deflect an electrometer.

The $\alpha$-rays cause zinc sulphide and some other substances to phosphoresce, and the number of $\alpha$-particles falling on a piece of zinc sulphide can be counted by watching the individual sparks or scintillations produced as each $\alpha$-particle strikes the screen. A screen of this kind, furnished with a magnifying lens, is known as a *spinthariscope.*

**1261. Theories of Radioactivity.**—It is believed (Chapter VII.) that the atom consists of a central nucleus of considerable mass surrounded by electrons distributed at distances, large compared with the dimensions of the nucleus. The nucleus contains protons and neutrons arranged in a manner which is still very uncertain. It is, at any rate, probable that certain stable 'parcels' of protons and neutrons exist as separate units within the nucleus. Rutherford

supposed, from considerations of the scattering of α-particles by the nucleus and the manner of its disintegration by α-particles, that it consists of an extremely minute and compact inner nucleus surrounded by a number of satellites. One of these 'satellites,' Rutherford believed, may become unstable (perhaps owing to some exceptional configuration of orbits) from time to time and may consequently fly off in the form of an α-particle. The β-particles, too, arise from the nucleus; it is thought that they are formed by a neutron changing into a proton, an electron, and a neutrino (§ 151c). There is as yet little certainty as to the structure of the nucleus, but it is clear that radioactivity consists of some kind of disintegration of the atomic nucleus. There is now a tendency to treat the nucleus from the point of view of the new wave-mechanics, rather than to try to form a picture of its structure.

The place of an element in the Periodic table (atomic number) is equal to its nuclear charge (§§ 141–145). Consequently the emission from the nucleus of an α-particle with a double positive charge ($He^{++}$) lowers the atomic number by two units (Table, p. 814). while the emission of one electron raises the charge and atomic number by one unit.

**1262. Preparation of the Radioelements.**—These elements are formed at a very slow rate from their original parents, uranium and thorium, and themselves decay comparatively quickly; consequently no uranium or thorium mineral contains more than a minute proportion of other radioelements. Thus, of a kilogram of uranium only about half a milligram would be transformed into uranium X in a hundred years, and as half of the uranium X present at any one time disappears in 24·6 days, it is clear that only the minutest amounts of this element can ever be present; the actual quantity being about ·000013 mg. If an element has a fairly long period, as radium has (1,580 years), it has a better chance of accumulating, and in an old uranium mineral there will be about 0·34 mg. of radium per kilogram of uranium element.

Some details as to the separation of a few of the radioelements and of their properties are given below.

**1263. Uranium I. and Uranium II.**—The chemistry of uranium is described on pp. 684–687. It always contains the isotope uranium II., which cannot be separated from it, and also uranium $X_1$, uranium $X_2$, uranium Y and uranium Z. Uranium $X_1$ may be separated from it by adding a rare-earth and precipitating it out with, say, oxalic acid. The insoluble oxalate is carried down with that of the rare-earth, although by itself the uranium $X_1$ is present in far too small quantity to be precipitated or filtered off.

**1264. Ionium.**—The chemistry of ionium is identical with that of thorium. It is obtained by separating 'thorium' from such uranium minerals as

contain very little of that element. It always contains thorium, which is inseparable from it.

**1265. Radium.**—This is the most important of the radioelements. It is prepared from uranium minerals in which there is about 1 gm. of radium per 3 tons of uranium, by the following method : The mineral is brought into solution with acids, etc., and the barium it contains is precipitated as sulphate, carrying down with it the radium, also as sulphate. The mixed sulphates are converted into the bromides by reduction, etc., and these are fractionally crystallised. Radium bromide is less soluble than barium bromide, and the crystals arising from each crystallisation contain more radium than the mother-liquor. Finally, a complete separation can be brought about. It is the tedious character of this process that brings about the high price of radium—a price which was at one period largely artificial and considerably above a reasonable figure for materials and labour.

Radium metal has been made by a method similar to that used for barium. Numerous salts have been prepared, including the hydroxide, chloride, bromide, sulphate, nitrate and carbonate. These resemble barium salts fairly closely, but are for the most part less soluble in water. The salts are unstable, being decomposed by their own radiation. In the same way radium bromide is decomposed, giving off bromine, and any water present is slowly decomposed into hydrogen and oxygen. The atomic weight of radium has been determined by the ratio $RaCl_2 : RaBr_2$, and by other means. The value 225·97 seems to be the most accurate.

**1266. Radon.**—Radium emanation is produced by radium. The dissolved gases are separated from a solution of a radium salt by pumping them off. They contain hydrogen and oxygen from the water, which gases are removed by explosion. The remaining gas is passed through a tube cooled by liquid air, where it solidifies. It is later allowed to evaporate and is sealed up in a tube. Preparations of radon are much used in experimental and medical work, as a practically unlimited succession of specimens may be obtained from a small quantity of radium. The radon decays to half its strength in four days. Radon boils at $-67°$ C. The feat of weighing about $\frac{1}{2}$ c.mm. of this gas has been performed and the density of the gas was thus found to be 111. Since the gas is presumably monatomic its atomic weight is 222.

**1267. Polonium.**—This element is an analogue of tellurium, but is present in such minute quantities that its chemical and physical properties cannot be readily studied. Despite the fact that a weighable quantity of pure polonium has not been obtained, it can be shown that it is precipitated with tellurium in some of the latter's reactions.

**1268. Thorium.**—The chemistry of this element is described on pp. 499–500. Its radioactivity is very feeble.

**1269. Mesothorium I.** is isotopic with radium and may be separated together with radium[1] from thorium minerals. Half of it decays in 6·7 years, and consequently only minute quantities are ever present, but these are very active.

**1270. Protoactinium Pa.**—The compounds of this element are isolated from radium residues. The element is grey-white and of metallic appearance. It does not oxidise in air. Its compounds resemble those of tantalum in general properties, but differ from it in that its pentoxide $Pa_2O_5$ is basic in character, while $Ta_2O_5$ is acidic. The element is precipitated as phosphate in acid solution, while tantalum is not so precipitated. It forms a chloride $PaCl_5$ as yellow needles easily sublimed and melting at 301° C. Its atomic weight has been determined by chemical methods as 230·6 $\pm$ 0·5.

The remaining natural radioelements are for the most part so transitory or are obtainable in such small quantities that their chemical properties cannot be ascertained.

**1271. Artificial Radioactivity.**—In the last ten years there has come about an astonishing development, the artificial production of radioactive isotopes of almost all the elements. The original discovery was made in 1934 by Mme. I. Curie and F. Joliot, who showed that certain elements, after exposure to $\alpha$-rays, themselves show radioactivity. Still more effective is the bombardment of elements with neutrons or with protons, deuterons, or $\alpha$-particles accelerated to very high velocities by means of the alternating electric and magnetic fields generated in the cyclotron.

The result, speaking in general terms, is that the nucleus of the bombarded atom absorbs the bombarding particle, so forming a new and unstable atom which then breaks down in the same manner as a natural radioelement. Such changes can be represented by equations in which the subscript figures represent nuclear charges and the superscript one atomic weights. Thus the fact that an isotope of iron bombarded with neutrons yields a radioactive form of manganese can be expressed by the equation as

$$_{26}Fe^{56} + {}_0n^1 \rightarrow {}_{25}Mn^{56} + {}_1H^1.$$

Some radioelements have been prepared in weighable quantities by bombardment with the cyclotron or in the uranium pile (v. *infra*). These include neptunium, plutonium, americium and curium (§ 1277), and also some radioactive isotopes, which owing to their high activity, have found a use as radium-substitutes, and as a means of ' ear-marking ' a quantity of a common element, so

[1] Thorium minerals always contain a little uranium.

that it may be distinguished from other portions of the same element. Thus if sodium phosphate containing radio-phosphorus, made by the bombardment of sodium phosphate with protons or deuterons, is administered to an animal, its bones become temporarily radioactive showing that there is a perpetual exchange of phosphate ions between the blood and the calcium phosphate of bone.

**1272. Effect of Neutrons upon Uranium.**—The study of the bombardment of uranium by neutrons has led to perhaps the most remarkable discovery of science, namely, the liberation of atomic energy. Uranium is a mixture of three isotopes U-238, U-235 and U-234 in the proportion 99·3 : 0·7 : 0·008.

When U-238 is bombarded by neutrons of a moderate energy-value it undergoes the process described in § 1271, forming a new nucleus, which emits an electron and produces

$$_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239} + \text{gamma rays}$$

$$_{92}U^{239} \rightarrow {}_{93}Np^{239} + {}_{-1}e^{0}$$

$$_{93}Np^{239} \xrightarrow{23\ \text{min}} {}_{94}Pu^{239} + {}_{-1}e^{0} + \text{gamma rays}$$

an element of atomic number 93 (neptunium), which by emitting a further electron forms element 94 (plutonium). These elements did not exist before these experiments. Some account of them is given in § 1277.

When U-238 is bombarded by neutrons of very high energy-value, or when either U-235 or plutonium is bombarded by neutrons of low energy value a different phenomenon takes place, which is known as nuclear fission. The nucleus of the atom splits into two parts of roughly equal mass and several high-energy neutrons are ejected. Each of these can cause another nucleus to split, and so a chain-reaction results by which a large mass of the material may be instantaneously decomposed with the liberation of enormous energy. The atomic weight of these elements is about 0·2 units higher than the sum of the atomic weights of the products of their fission. Thus when a gram-atom of one of these elements decomposes about 0·2 gms. of mass are converted into about $0{\cdot}2 \times (3 \times 10^{10})^2$ ergs (§ 30) which amount of energy is equivalent to about six million horse-power hours.

Thorium behaves in this respect like U-238, and protoactinium in a fashion intermediate between that of U-238 and U-235.

**1273. Practical Utilisation of Atomic Energy.**—A chain-reaction such as is described above cannot be maintained in U-238 because most of the neutrons are absorbed to form U-239 which ultimately gives plutonium. It can however be maintained in U-235 or in

plutonium; or in mixtures of U-238 and U-235, provided certain conditions are observed. It cannot proceed in presence of any considerable quantity of impurity, *i.e.* atoms that very readily absorb neutrons, but do not undergo fission. To bring about the explosive liberation of energy it is only necessary to bring together a number of small portions of these elements. Small portions do not explode because the majority of neutrons escape without causing fission, but a piece of metal above a certain size, not yet disclosed, will arrest enough of these to cause the chain-reaction to take place.

Success has been attained (1) by separating U-235 from natural uranium; (2) by the artificial preparation of plutonium.

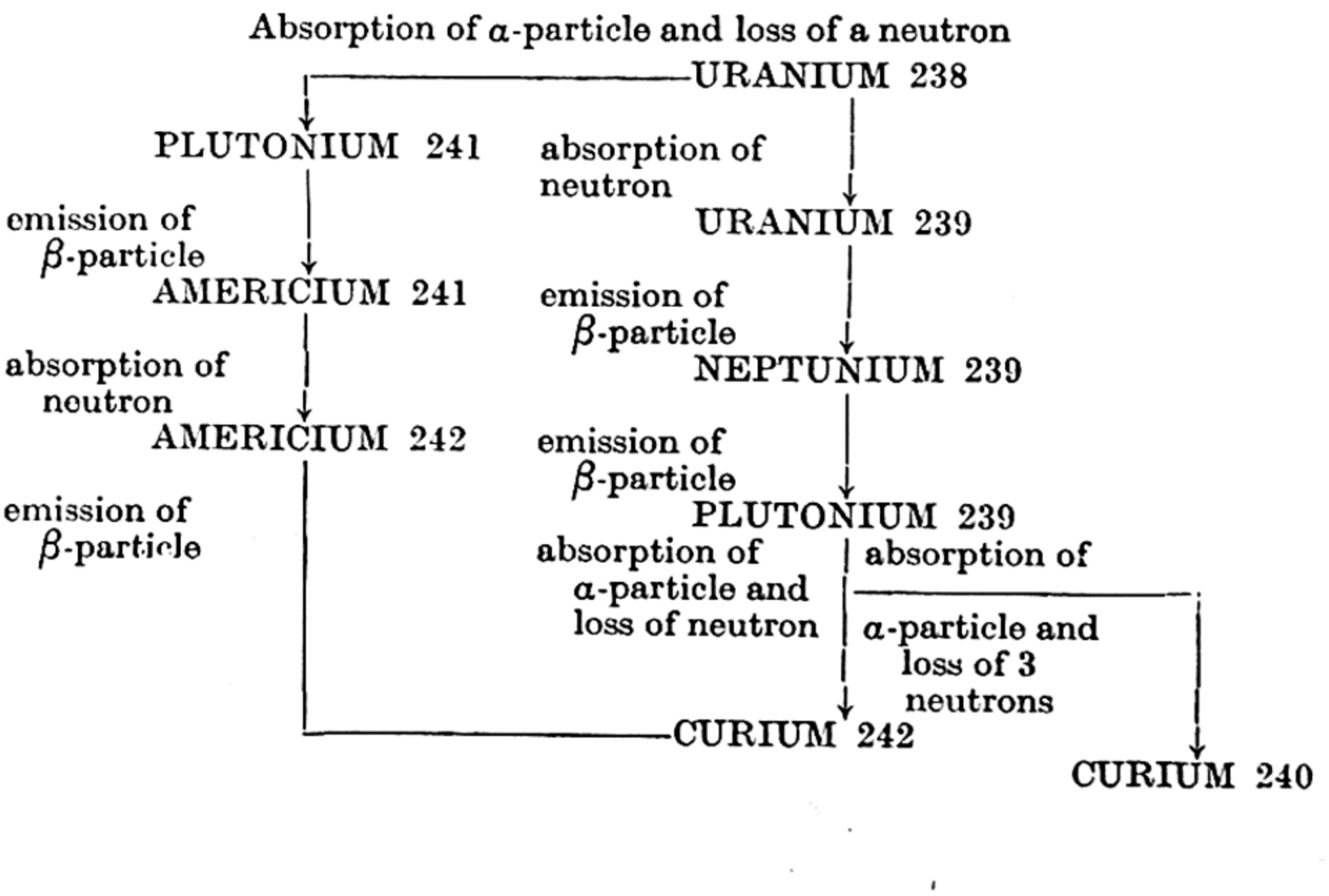
**1274. Separation of U-235 from Uranium.**—The great difficulty of separating isotopes is indicated in §§ 149, 150; and the separation of a small quantity of an isotope of high atomic weight is a most unfavourable case. The use of thermal diffusion on volatile compounds of uranium was, however, effective enough to allow of the extraction of a sufficient quantity of U-235 to explode. For this purpose the separation need not be complete. The method was however enormously costly and laborious; consequently it is now discarded in favour of the making of plutonium.

**1275. Conversion of U-238 into Plutonium.**—Uranium is first of all very highly purified from other elements, but is not separated into isotopes. It is then formed into rods encased in thin aluminium shells. These are embedded in very pure graphite or immersed in heavy water (§ 193a). "Piles" of uranium rods and graphite, containing many tons, are built up, and are screened by heavy concrete walls to protect the workers from the intense radiation produced. The pile is bombarded by a weak neutron source (radium + beryllium) which serves to start the reaction. Some U-235 atoms undergo fission; some of the neutrons from these break up further U-235 atoms but the greater part are slowed down by collisions with the atoms of the graphite (or heavy water), and, as described in § 1272, are absorbed by the U-238 which finally forms plutonium. This process continues indefinitely. The pile produces vast quantities of energy, which it is hoped to use as a source of power; the principal difficulty being the need to prevent the temperature from rising, which raises the problem of utilising vast amounts of low temperature heat. A heat-resistant casing is now said to have been invented, which will allow the piles to run at higher temperatures. The uranium is removed mechanically from time to time and the plutonium is separated by chemical processes. Owing to the quantities of radioactive substances present, the extraction has to be conducted automatically and without direct supervision.

**1276. Future of Atomic Energy.**—When mass is converted into energy 1 gm. produces $9 \times 10^{20}$ ergs, and if matter could be wholly converted into energy the problem of power-supply would be completely solved. It must be noted, however, that of the mass of U-235 or plutonium only a small fraction—about one-thousandth—is thus utilised, being the difference between the atomic weight of these elements and the total atomic weights of their products of fission, elements and neutrons. As far as we know no particle is annihilated in this process, and the mass that is lost is simply the mass that was gained through packing the ultimate particles into nuclei (§ 149). So the only elements that could yield atomic energy are those with a large packing-fraction, i.e. the few elements at the beginning and end of the periodic table. The synthesis of heavier elements from hydrogen would give enormous energy, but the indications are that it will take place only at temperatures of the orders of $10^7$°C., which have not as yet been achieved. At present, therefore, the discovery of sources of atomic energy more effective than uranium is only a theoretical possibility.

**1277. Transuranic Elements.**—Four elements of atomic number higher than that of uranium are now known. These exist in several isotopic forms with different nuclear properties (i.e., radioactivity and power of fission).

All have been isolated in weighable quantities. These four elements are neptunium, Np ; plutonium, Pu ; americium, Am, and curium, Cm. The first two are made by bombardment of uranium with neutrons in the pile (§ 1272), the last two by bombardment of uranium and plutonium with alpha-particles in the cyclotron. The following scheme indicates their mode of formation.



Their nuclear properties are summarised in the following scheme:—

| ELEMENT | AT. NO. | ISOTOPES | NUCLEAR PROPERTIES |
|---|---|---|---|
| Neptunium | 93 | 237 | decays emitting $\alpha$-particle to isotope of proto-actinium. |
| | | 238, 289 | decay emitting $\beta$-particles to plutonium. |
| Plutonium | 94 | 241 | decays emitting $\beta$-particle to americium. |
| | | 240 | not fully investigated. |
| | | 239 | fissionable; bombardment with $\alpha$-particles and neutrons gives curium. $\alpha$-particle decay to U–235 (30,000 years). |
| | | 238 | decays to uranium emitting $\alpha$-particle. |
| | | 242 | $\beta$-particle decay to curium. |
| Americium | 95 | 241 | $\alpha$-particle decay to neptunium. |
| | | 242 | $\alpha$-particle decay to plutonium, not fully investigated. |
| Curium | 96 | 240 | |

Of these elements neptunium has been obtained in the pure state in quantities of several hundred milligrams, plutonium in kilograms, americium and curium in quantities of *c.* 1 mg. The chemistry of all of these has been investigated, though there is great difficulty in dealing with the last two owing to their intense radioactivity. All four elements resemble uranium and seem to be the beginning of a period such as that of the rare earths in which a sub-group in the fifth quantum group is being filled up.

Their chief difference from uranium is that their ions of lower valency, 3 and 4, are more stable than U III and U IV ions, while those in which the element has valency 6 are less stable than $UO_2^{++}$.

## QUESTIONS

(The atomic weights of the table on p. 838 have been used throughout.)

### Chapter IX

(1) In what respects is hydrogen an exceptional element ? Where should it be placed in the Periodic table ?

(2) Describe and explain the electrolytic methods of obtaining hydrogen.

(3) Under what conditions is hydrogen a valuable reducing agent ? How can it be used to reduce (*a*) metallic oxides, (*b*) ethylene, (*c*) ferric salts in solution ?

(4) State Graham's law and describe experiments illustrating it. One hundred cubic centimetres of oxygen escape through a small hole in ten minutes. What volume of hydrogen would escape in the same time and under the same conditions ?

(5) One gram of hydrogen burning to liquid water evolves 33900 cals. One gram of hydrogen sulphide burning to liquid water and sulphur dioxide evolves 4020 cals. If 2293 cals. are evolved then one gram of sulphur burns to sulphur dioxide, what is the heat of formation of hydrogen sulphide ?

(6) How has it been established that the ratio of the atomic weights of oxygen and hydrogen is 16·000 : 1·0080 ?

(7) On what grounds is the formula of water taken to be $H_2O$ ?

(8) In what respects does the chemistry of hydrogen resemble that of a metal ?

(9) In what respects is water exceptional among chemical compounds ? Comment on its use as a solvent in inorganic chemistry.

(10) What steps have to be taken to prepare from impure water (*e.g.*, river water) :

(*a*) Sanitarily pure water for household use.

(*b*) Soft water for washing, etc.

(*c*) Water pure enough for chemical analysis.

(*d*) Water of very high purity for conductivity experiments.

(11) Describe the preparation of hydrogen peroxide. Comment on its action: (*a*) as an oxidising agent ; (*b*) as a deoxidising agent.

(12) Make a list of the various substances which go by the name of hydrogen and indicate the conditions under which they can exist.

(13) Describe the industrial preparation of hydrogen and indicate its industrial uses.

(14) What are the typical reactions of water with (1) elements ; (2) oxides ; (3) salts ?

### Chapter X

(1) Compare the reactions of metallic sodium with those of zinc. How far is it possible to account for the difference between the behaviour of the two metals ?

(2) Describe the manufacture of caustic soda. How would you test for the presence of carbonates and chlorides in commercial caustic soda ? How could they be removed if present ?

(3) In a certain experiment 4·1400 gms. of pure sodium chloride were converted into 5·0302 gms. of sodium sulphate. What value for the equivalent of sodium does this indicate ? What further evidence enables us to arrive at the atomic weight ?

(4) It was found experimentally that 2·0517 gms. of potassium bromide precipitated from solution 3·2375 gms. of silver bromide. What is the atomic weight of potassium, if it be assumed that the element is monovalent ?

(5) Explain the principles underlying the Solvay process for the manufacture of sodium carbonate.

(6) How is potassium nitrate prepared from sodium nitrate ? Explain the procedure adopted.

(7) Why are sodium, potassium and ammonium salts used to a greater extent than those of other metals in chemical work, both experimental and industrial ?

(8) What industrially important products are derived from sodium chloride ? Explain shortly the methods of manufacturing these.

(9) In what respects do the oxides and hydroxides of the alkali metals differ from those of other metals ?

(10) How would you try to find out whether a hydrated form of common salt existed at low temperatures and how would you discover its formula ?

(11) Why do solutions of sodium carbonate have many of the properties of alkalies ? What other salts manifest similar phenomena ?

(12) Classify the various types of reaction that elements undergo in contact with sodium hydroxide or its solutions.

(13) What sodium and potassium salts are not commonly made by the action of the acid on the hydroxide of the metal ? Give equations and summarised conditions for the preparation of these salts.

## Chapter XI

(1) The elements of Group I. B resemble those of Group VIII. rather than those of Group I. A. Discuss and explain this statement.

(2) What is meant by the term ' noble metals ' ? Compare the properties of a typical noble metal, such as gold, with those of a typical ' heavy metal ' *e.g.*, lead.

(3) How would you prepare specimens of cupric chloride and cuprous chloride ? How far are the differences between them of the same type as the differences between ferrous and ferric chlorides ?

(4) Explain why insoluble compounds of copper and silver are dissolved by (*a*) ammonia solution, (*b*) solutions of cyanides.

(5) Why are the methods used for obtaining copper from its ores not applicable to (*a*) silver, (*b*) iron ?

(6) Explain the principles underlying the methods you would use to find the proportions of silver and copper in a modern British sixpence containing silver, copper, zinc and nickel.

(7) To what purpose has the electrolysis of solutions of copper, silver and gold compounds been applied ? Explain the principles which underlie the method used to obtain a coherent layer of metal.

(8) To some silver nitrate solution is added ammonia until the brown precipitate at first formed redissolves. A little formaldehyde is added and

the solution is warmed. A brilliant mirror forms on the vessel. Explain fully what has occurred.

(9) Twenty cubic centimetres of a solution of 5 gms. of a copper salt in 250 c.c. of water were added to an excess of potassium iodide solution, and the resulting solution was titrated with $N/10$ sodium thiosulphate, 33·5 c.c. of which were required to react with the iodine liberated. Calculate the percentage of copper in the salt.

(10) By what methods is silver obtained as a by-product in the making of (*a*) lead ; (*b*) copper ?

(11) What methods are used for the preparation of cuprous salts ? How would you prepare in the laboratory cuprous oxide from metallic copper ?

(12) What is meant by a colloidal metal ? Describe two ways of preparing colloidal silver. What precautions are especially necessary for success ?

## Chapter XII

(1) What calcium and magnesium compounds are commonly present in tap-water ? Why are the compounds of these metals commonly present and those of other metals but rarely ? Explain the principles employed for their removal.

(2) Some calcium carbonate is sealed up in a strong evacuated tube which is then heated to about 800° C. What happens ? What would happen (*a*) if the pressure in the tube were kept at *c.* 1 mm. of mercury by means of a pump, (*b*) if the tube had been filled with carbon dioxide before sealing ?

(3) In what respects do barium and its compounds differ from calcium and its compounds ? How could you prepare pure barium and calcium chlorides from a mixture of the carbonates of barium and calcium ?

(4) What are (*a*) plaster of Paris, (*b*) Portland cement, (*c*) mortar ? How are they made and why do they set ?

(5) Compare the properties of magnesium with those of its neighbours in the Periodic table, sodium and aluminium. What conclusions are to be drawn ?

(6) The specific heat of calcium metal is 0·152. 10·084 gms. of calcium carbonate were converted into 20·142 gms. of anhydrous calcium bromide. Without *assuming* the formula of any calcium compound, calculate the atomic weight of calcium.

(7) One hundred cubic centimetres of a saturated solution of slaked lime required 5·7 c.c. of $N/2$ hydrochloric acid to neutralise it. Calculate the solubility of slaked lime.

(8) What are the industrial uses of magnesium ? Describe the methods used for its industrial preparation.

(9) How is calcium carbide made ? What industrially important compounds are made from it, and how ?

## Chapter XIII

(1) Compare the advantages of galvanising, painting and tin-plating as means of preserving iron from rust.

(2) Give examples of the use of zinc and acid as a reducing agent. What weight of zinc would theoretically be required to reduce 10 gms. of potassium

dichromate $K_2Cr_2O_7$ in solution in dilute hydrochloric acid to chromous chloride $CrCl_2$ ? Why would more zinc than this be needed in practice ?

(3) Compare the action of magnesium, zinc and mercury on acids. Explain the differences you note.

(4) In what important respects do the salts of mercury differ from those of all other common metals ? Two copper plates are connected to an ammeter and accumulator, and are immersed in a solution of mercuric chloride, which is well stirred. Explain what occurs and give a reason for the large increase which appears in the ammeter reading as the experiment progresses.

(5) Devise a method for separating the constituents of an amalgam containing zinc, cadmium and mercury, based on the differing solubility of the sulphides of these metals.

(6) Describe the industrial preparation and laboratory purification of mercury.

(7) How is mercury converted into (*a*) mercuric chloride; (*b*) mercurous chloride; (*c*) mercuric oxide? Explain what is observed when an excess of potassium iodide is gradually added to a solution of mercuric chloride.

(8) Describe the industrial preparation of pure zinc. How would you convert this in the laboratory into anhydrous zinc chloride ?

## Chapter XIV

(1) Compare the properties of boron and aluminium. In what respects does boron also resemble carbon ?

(2) How is borax prepared from native calcium borates ? Explain the fact that borax may be titrated with dilute acids.

(3) In what respects does the chemistry of aluminium and its compounds resemble that of a non-metal ? Compare its properties with those of its neighbours, magnesium and silicon.

(4) Explain the following phenomena :

(*a*) Sodium aluminate when boiled with ammonium chloride solution precipitates all its aluminium as hydroxide.

(*b*) Aluminium chloride solution boiled with sodium thiosulphate gives a precipitate of aluminium hydroxide. What other products would you expect ?

(5) What is an alum ? Explain how you would try to find out whether a metal of which the sulphate was available would form an alum.

(6) Discuss the relationship of the rare earths to the other elements and their consequent position in the Periodic table.

(7) Metallic aluminium, though strongly electropositive is comparatively unreactive. Discuss this fact and account for it.

(8) How is aluminium made on the industrial scale ?

(9) Describe the preparation of anhydrous aluminium chloride. Discuss its formula and indicate its importance as a laboratory reagent.

(10) How would you prepare a specimen of boric acid from ordinary borax. What is the theoretical yield from 100 gms. of borax ?

## Chapter XV

(1) On what grounds are diamond and graphite regarded as the only true allotropic forms of carbon ? How could it be proved that graphite and diamond are identical in chemical composition ?

(2) In what respects are the properties of charcoal remarkable and how have they been applied ?

(3) In what respects does the chemistry of carbon differ from that of silicon ?

(4) Why are carbon monoxide and ethylene both said to be unsaturated ?

(5) How would you demonstrate the presence of (*a*) hydrogen, (*b*) methane, (*c*) ethylene in a specimen of coal gas ?

(6) Write a short essay on the importance of carbon dioxide in biological and geological phenomena.

(7) Twenty-five cubic centimetres of *N*/50 barium hydroxide rendered pink with phenolphthalein were shaken in a bottle containing 5 litres of air at 20° C. and 700 mm. pressure. Twenty cubic centimetres of *N*/50 HCl were required to decolorise the solution. Calculate the percentage of carbon dioxide (by volume) in the air.

(8) Acetylene is an endothermic compound. What does this mean and what steps would you take to confirm it experimentally ?

(9) What is a flame ? On what does its luminosity depend ? Illustrate the structure of a luminous coal-gas flame, account for its structure and indicate the chemical reactions which occur in the various parts of it.

(10) What gases derived from coal or its products are made on the industrial scale ? Give their approximate composition.

(11) How are carbon monoxide and carbon dioxide made (*a*) in the laboratory ; (*b*) industrially ? What are their industrial uses ?

(12) Compare the properties of carbon dioxide and carbon monoxide. What other oxides does the latter most resemble and does this resemblance extend to their formulæ ?

## Chapter XVI

(1) What are meant by the terms *sol* and *gel* ? Illustrate your answer by reference to silicic acid. What steps would you take to ascertain whether silicic acid had the formula $[Si(OH)_4]_n$, $[OSi(OH)_2]_n$ or $[SiO_2xH_2O]_n$ ?

(2) Compare and contrast the properties of the halides of the elements of Group IV. B.

(3) For what purposes can stannous compounds be used as reducing agents ? How would you find out whether the reaction of an acidified solution of stannous chloride with a solution of iodine was complete or not ?

(4) " Quadrivalent tin is non-metallic, bivalent tin is metallic." Discuss this statement.

(5) Compare the properties of the oxides of tin and of lead.

(6) Iron is protected by coating it with tin or with zinc. Discuss the merits of the two systems. Cadmium plating is now occasionally used. Cadmium is not precipitated by the action of metallic iron on its salts. In view of this fact and the position of cadmium in the Periodic table, what advantages is cadmium plating likely to present ?

(7) Explain the method used to detect tin in a mixture of its salts with those of other metals. Why is stannous sulphide soluble in yellow but not in colourless ammonium sulphide ?

(8) At 200° C. and atmospheric pressure 0·203 gm. of stannic chloride vapour occupy 30·2 c.c. Stannic chloride contains 54·4 per cent. of chlorine. What is the most probable value for the atomic weight of tin as indicated by these figures ? State what facts you assume (Cl = 35·46).

(9) Explain the construction and principles of the lead accumulator.

(10) How is lead prepared from galena ? What are the chief industrially useful compounds of lead? Describe the preparation of each.

(11) What experiments would you carry out in order to discover the composition of specimens of (*a*) red lead; (*b*) white lead ?

(12) Describe and explain the chief differences between the chemistry of tin and lead.

## Chapter XVII

(1) Discuss the economic importance of combined nitrogen.

(2) How far is it correct to call nitrogen and inert element ?

(3) What analogies are to be traced between the simplest hydrides of nitrogen, phosphorus and oxygen respectively ? In what respect are all of them in contrast to methane ?

(4) What action has ammonia on metallic salts, both solid and in solution ? Illustrate your answer by the cases of the chlorides of sodium, calcium, magnesium, zinc, iron, copper and silver.

(5) How may pure nitric oxide be prepared ? Discuss its structure in view of its reactions. What resemblances does it show to carbon monoxide ?

(6) What functions has nitric acid in chemical work ? Compare its chemical behaviour with that of sulphuric acid.

(7) What reactions occur when a mixture of nitrogen peroxide with an excess of oxygen is brought into intimate contact with cold and hot water respectively ?

(8) In what manner will the variation of the volume of nitrogen peroxide with changes in temperature and pressure deviate from that indicated by Boyle's law ? A specimen of the gas shows a vapour density, relative to hydrogen at the same temperature, of 36·8. Calculate the proportion of $NO_2$ by volume present in the gas.

(9) How do the products of the reaction of nitric acid with metals and other reducing agents depend on (*a*) the character of the reducing agent, (*b*) the dilution of the acid ?

(10) The densities relative to hydrogen of certain volatile compounds containing nitrogen are as follows : ammonia 8·5, nitrous oxide 22, nitric oxide 15, nitrogen 14. Ammonia contains 17·65 per cent. of hydrogen. Without assuming any formulæ, deduce the atomic weight of nitrogen.

(11) What methods have been used for the synthesis of nitrogen compounds from the atmosphere ?

(12) How is ammonia prepared industrially by direct synthesis ? Explain the principles which determine the temperature and pressure at which the reaction is carried out.

(13) How can the formula of ammonia gas be established ? What do you suppose to be present in a solution of ammonia and why ?

(14) Describe the action of heat on ammonium salts. What gases are evolved and from what types of salt ?

(15) How would you prepare a specimen of pure dry nitrous oxide. In what respects do its properties resemble and differ from those of oxygen ?

(16) Describe the preparation of nitrous acid. Under what conditions is it oxidised and reduced and what are the products. How would you detect the presence of a minute proportion of nitrite in a specimen of water ?

## Chapter XVIII

(1) What likenesses and differences are to be seen in the allotropy of the elements of Group V. B ?

(2) Discuss the phenomena which attend the oxidation of phosphorus.

(3) In what respects do the compounds of phosphorus resemble those of nitrogen ?

(4) What agricultural importance has phosphorus ? Why is it necessary to supply phosphorus to the soil ? In what forms is it supplied and what are the advantages of the respective forms ?

(5) Discuss the structure of the molecules of the oxyacids of phosphorus, particularly with reference to their basicity.

(6) Explain the principle of the method you would employ to detect the presence of a minute proportion of arsenic in a food-stuff.

(7) Explain what happens when antimony sulphide is dissolved in yellow ammonium sulphide.

(8) Freshly precipitated antimony sulphide is dissolved in an excess of diluted hydrochloric acid. On dilution of a portion of the solution an orange precipitate appears. A part of the solution is boiled for some minutes and then diluted. A white precipitate is formed which redissolves on addition of more acid. Explain these phenomena.

(9) Compare the properties of the elements bismuth and lead. How would you detect the former in presence of the latter ?

(10) Compare and contrast the properties of the elements of Group V. B. In what respects do (*a*) nitrogen; (*b*) bismuth differ from the rest and how is this accounted for ?

(11) How is phosphorus made industrially ? How can red phosphorus be made into yellow phosphorus and *vice versa* ? How would you detect the presence of some yellow phosphorus in a specimen of red ?

(12) Give the formulæ of all the substances which go under the name of sodium phosphate. How could each of them be made from phosphorus ?

(13) How can phosphorus be converted into each of its chlorides ?

(14) Why is the formula $PH_3$ assigned to phosphine? In what respects does it resemble and differ from ammonia?

## Chapter XIX

(1) What methods can be used to determine the proportion of oxygen in a mixture of gases ? How could the proportion of free oxygen in a mixture of (*a*) air and nitrous oxide, (*b*) oxygen and carbon dioxide be determined ?

(2) Explain the function of oxygen in the animal body. How would you attempt to discover whether a specimen of arterial blood gave off oxygen when subjected to reduced pressure ?

(3) How are the oxides of the elements classified ? To what category are assigned magnesium oxide, lead dioxide, barium dioxide, water, red lead ?

(4) How is oxygen converted into ozone ? One thousand cubic centimetres of ozonised oxygen were shaken with a weakly acid solution of potassium iodide. The solution of iodine so obtained was decolorised by 22·7 c.c. of $N/10$ sodium thiosulphate solution. Calculate the weight of ozone in the original gas mixture.

(5) On what grounds is the formula of ozone taken to be $O_3$ ?

## Chapter XX

(1) In what forms does sulphur exist and which of them are true allotropes ? Explain by means of a diagram the conditions under which they are permanently stable.

(2) How would you prove that a specimen of monoclinic sulphur was identical in composition with a specimen of amorphous sulphur ?

(3) What analogies can be traced between the chemistry of the elements oxygen and sulphur ?

(4) How do the sulphides of the metals react with (i.) water, (ii.) acids, (iii.) sulphides of the alkali metals and ammonium ? Explain how the above reactions are made the basis of a system of quantitative analysis.

(5) What resemblances and what differences are to be found in the chemical behaviour of water and hydrogen sulphide ?

(6) How may sulphur be converted into sulphuric acid ? What weight of the latter could be made from 1 gm. of sulphur ? How would you verify your result experimentally ?

(7) By what substances can sulphur dioxide be converted into sulphuric acid ? Which of these methods are of industrial importance and why ?

(8) What grounds have we for believing that sulphurous acid is contained in a solution of sulphur dioxide ? What evidence exists as to the structure of the molecule of sulphurous acid and the sulphites ?

(9) What effect has iodine upon the salts of the various acids of sulphur and what information as to their structure can be gained therefrom ?

(10) Describe the behaviour of sulphuric acid towards water. When is the acid suitable as a drying agent and when unsuitable ?

(11) How is the reaction between sulphur dioxide and oxygen affected by temperature and by catalysts ? How is it utilised industrially ?

(12) Discuss the question as to whether the phenomena which occur when sulphuric acid combines with water indicate a chemical change.

(13) Describe the Frasch process for obtaining sulphur. What other natural sources of sulphur compounds exist and how are they utilised ?

(14) What compounds of sulphur are commonly used as reducing agents ? Give details of typical reactions and indicate the particular advantages of each compound referred to.

(15) Describe the preparation of (*a*) thionyl chloride; (*b*) sulphuryl chloride; (*c*) chlorosulphonic acid. How do these react with compounds containing hydroxyl groups ?

## Chapter XXI

(1) How would you convert a specimen of chromic chloride into (i.) potassium chromate, (ii.) potassium dichromate, (iii.) chromous chloride ?

(2) In what respects do the chromic salts resemble and differ from those of aluminium ?

(3) Give examples of the use of chromic acid and its salts as oxidising agents and explain any advantages they present over other oxidising agents.

(4) What is chrome alum and why is it so called ? 1·5 gms. of chrome alum are fused with caustic soda and some potassium nitrate and the resulting solid taken up with water and made acid with dilute sulphuric acid. What weight of

iodine would be liberated on addition of this solution to an excess of potassium iodide ?

(5) What analogies are to be detected between the chemistry of chromium and of sulphur ?

(6) Describe the industrial preparation and uses of chromium. Describe and explain its industrial importance.

(7) Chromium is so named from the varied colours of its compounds. Under what conditions can purple, green, pale blue, yellow and orange solutions of chromium salts be obtained and what ions do they contain ?

(8) How would you prepare chrome alum from chromium trioxide ?

(9) Discuss the resemblance of the acids and salts of sexavalent chromium to those of sulphur.

## Chapter XXII

(1) Compare and contrast the properties of the halogen elements. Hydrogen has sometimes been placed at the head of the halogen group. How far is this justifiable ?

(2) In what ways is fluorine exceptional among the halogen elements ?

(3) A very pure and dry specimen of chlorine is required for the measurement of one of its physical properties. How would you prepare it ?

(4) Discuss the phenomena which attend the combination of the halogen elements with hydrogen.

(5) The halogen elements are useful oxidising agents. Give examples of their use and point out their advantages over other oxidising agents for the oxidations you describe.

(6) A solution of hydrogen chloride is prepared by saturating water at 0° C. with the gas. What will happen to such a solution when it is (i.) heated as long as any further change takes place, (ii.) strongly cooled ?

(7) Explain the conditions under which the reaction of common salt and sulphuric acid yields hydrogen chloride. How is it ultilised on the commercial scale ?

(8) How are the potassium salts of the oxyacids of chlorine prepared ? What happens when (*a*) potassium hypochlorite, (*b*) potassium chlorate are heated ?

How far do reactions analogous to those described take place with the other halogens ?

(9) What difficulties attend the preparation of pure hydrogen bromide and pure hydrogen iodide ? How would you prepare the former gas and determine its solubility in water ?

(10) How are the reactions of iodides with oxidising agents utilised in volumetric analysis ? 1·5 gms. of a mixture of potassium chloride and potassium chlorate were dissolved in a little water and acidified with hydrochloric acid. An excess of potassium iodide solution was added and the solution was made up to 500 c.c. Twenty cubic centimetres of this required 21·0 c.c. *N*/10 sodium thiosulphate to decolorise it. Calculate the percentage of potassium chlorate in the mixture.

(11) How would you prepare a specimen of iodic acid ? How would it react with solutions of (i.) potassium iodide, (ii.) sulphur dioxide ?

(12) How is iodine manufactured ? How would you recover pure dry iodine from a solution containing iodides and various other salts ?

(13) Make a list of the oxides of chlorine and give methods for the prepara-

tion of the gaseous oxides. How would you investigate the composition of an unknown oxide of chlorine ?

(14) What is bleaching-powder ? How is it made and how can its value for bleaching and other purposes be determined ?

(15) Compare and contrast the fluorides, chlorides, bromides and iodides. How could you discover the presence of each of these in a mixture of all four ?

## Chapter XXIII

(1) How would you prepare a specimen of pure manganese dioxide starting from manganous sulphate ? How would you convert the product into potassium permanganate ?

(2) How would you test the purity of a specimen of potassium permanganate ? In purifying it by recrystallisation, what precautions would have to be taken ?

(3) A stream of hydrogen sulphide is passed through a neutral solution of potassium permanganate. The solution deposits a dark brown precipitate, which then becomes pale pink. On addition of acid most of the precipitate dissolves, leaving in suspension a white solid, which does not readily settle out. Explain these phenomena.

(4) 1·5 gms. of a reducing agent were dissolved to form 100 c.c. of solution. Ten c.c. of this solution decolorised 14 c.c. of $N/10$ potassium permanganate. Calculate the oxygen equivalent of the reducing agent.

(5) Compare the manganates and permanganates with the chromates and dichromates.

(6) In what respects is manganese analogous to the halogens on the one hand and chromium and iron on the other ?

(7) How does potassium permanganate react with reducing agents in presence of acid and alkali respectively? Given pure dry potassium permanganate, how would you estimate the proportion of iron in a specimen of native ferrous carbonate ?

## Chapter XXIV

(1) What chemical principles underly the extraction of iron from its ores and its subsequent conversion into steel ?

(2) Discuss the rusting of iron and the means used to prevent it.

(3) How may ferrous compounds be converted into ferric compounds and *vice versa* ? How have these processes been applied to chemical analysis ?

(4) "Ferric hydroxide is a weaker base than ferrous hydroxide." Substantiate this statement.

(5) Ferric oxalate is reduced in presence of light to ferrous oxalate. How would you substantiate this statement, investigate the reaction and try to discover whether the amount of reduction was proportional to the quantity of light absorbed ?

(6) Why is anhydrous ferric chloride not prepared by heating the hydrated salt ? Describe the usual method for its preparation.

(7) Describe and explain methods which would enable you to detect traces of (i.) iron in common alum, (ii.) ferric sulphate in ferrous sulphate, (iii.) ferrous chloride in ferric chloride.

(8) Cobalt is placed between iron and nickel in the Periodic table, though the atomic weights indicate the order as iron, nickel, cobalt. Why is the former order adopted and how is this departure from the usual order justified ?

(9) What is a 'carbonyl' ? How has the formation of such a compound been used in the preparation of pure nickel ?

(10) Discuss the catalytic activity of the metals of Group VIII.

(11) Why cannot pure anhydrous ferric and ferrous chlorides be made by the methods adopted for the preparation of most chlorides ? How would you make a small specimen of each of these ?

(12) What is iron alum ? How would you make a pure specimen and why is it a useful volumetric standard ?

## Chapter XXV

(1) What researches led to the discovery of the group of inert gases ? How would you attempt to prepare a specimen of argon, using only the apparatus available in an ordinary school laboratory ?

(2) Explain the chemical inertness of the gases of Group 0. In what ways have they been utilised industrially ?

(3) On what grounds are the inert gases believed to have their accepted atomic weights ?

## Chapter XXVI

(1) What is meant by a radioactive transformation ? What evidence can be adduced that uranium is being transformed into other elements ?

(2) What is the 'half-period' of a radioactive element ? How is this quantity determined experimentally ?

(3) Discuss the relationship between radioactive changes, the structure of the atom, and the Periodic table.

(4) Describe the types of transmutations which have been brought about by atomic bombardment, and explain the principles underlying the practical liberation of atomic energy.

## Miscellaneous Questions

(1) How and by whom was it first established that (*a*) air, (*b*) water, was not a chemical element in the modern sense ?

(2) Give three instances of the chemical action of light which have been used in photography. Explain what takes place when an ordinary film is exposed, developed and fixed.

(3) What are the chief inorganic sources of plant-food ? Briefly summarise the manner in which these are manufactured as fertilisers.

(4) Classify the methods used for extracting metals from their ores. To which classes of metals are each of these specially applicable ?

(5) What general methods are applicable to the purification of chemical substances ?

(6) Tabulate the facts concerning the reaction of the three common mineral acids with the various classes of metals.

(7) What is meant by " transition elements" ? What properties are common to the transition elements of the first long period and their compounds ?

(8) Do you consider that iron, cobalt and nickel should be placed in a single group of the periodic table ?

(9) Define the terms " oxidation " and " reduction ". Give an example of a compound that can act both as a reducing and an oxidising agent. How do you explain the oxidising and reducing actions of an electrolytic cell ?

(10) What are peracids ? A washing powder contains some sodium perborate : how would you attempt to discover the proportion present ?

(11) Classify the types of hydride formed by the chemical elements. In what respects is methane exceptional ? Can you explain this ?

(12) Write a short essay on the corrosion of metals, referring particularly to the case of iron.

(13) Give the whole argument by which it can be proved that the formula of water is $H_2O$, making no assumptions other than those of the atomic theory.

(14) Write an essay on the discovery of the composition of air. Do you think it possible that air still contains an undiscovered permanent constituent ?

(15) What is meant by an acidic oxide ? Illustrate your answer by brief reference to the oxides of nitrogen, phosphrous sulphur and chlorine. Are there any acidic oxides without a corresponding oxy-acid or *vice-versa* ?

(16) Classify the properties of sulphuric acid under suitable headings. Name substances which possess each of these sets of properties.

(17) To what purposes are aluminium, zinc, iron, chromium put in industry and how do these depend upon their chemical and physical properties ?

(18) How were the inert gases discovered ? Describe their extraction and industrial uses.

(19) Elements are often said to exist in more active forms. Explain the nature of these, referring to the cases of hydrogen, nitrogen, oxygen, phosphorus in the course of your answer.

(20) Compare and contrast the work of Priestley and Lavoisier.

(21) What chemical manufacturing processes were made possible by the availability of electricity supplies from about 1880 onwards ?

## ANSWERS TO NUMERICAL EXAMPLES

Chapter IX.—4. 400 c.c.
5. 4496 cals.
Chapter X.—3. 23·00.
4. 39·01.
Chapter XI.—9. 53·24 per cent.
Chapter XII.—6. 40·09.
7. 0·1056 gms./100 c.c.
Chapter XIII.—2. 8·89 gms.
Chapter XV.—7. 0·0247 per cent.
Chapter XVI.—8. 118·9.
Chapter XVII.—8. 40·9 per cent.
10. 14·00.
Chapter XIX.—4. 0·0545 gms.
Chapter XX.—6. 3·059 gms.
Chapter XXI.—4. 1·1434 gms.
Chapter XXII.—10. 71·49 per cent.
Chapter XXIII.—14. 107·14.

# ATOMIC WEIGHTS, 1949

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Atomic weights in brackets denote the mass number of the most stable known isotope.

| Atomic number | Name | Symbol | Atomic weight | Atomic number | Name | Symbol | Atomic weight |
|---|---|---|---|---|---|---|---|
| 1 | Hydrogen | H | 1·0080 | 49 | Indium | In | 114·76 |
| 2 | Helium | He | 4·003 | 50 | Tin | Sn | 118·70 |
| 3 | Lithium | Li | 6·940 | 51 | Antimony | Sb | 121·76 |
| 4 | Beryllium | Be | 9·013 | 52 | Tellurium | Te | 127·61 |
| 5 | Boron | B | 10·82 | 53 | Iodine | I | 126·92 |
| 6 | Carbon | C | 12·010 | 54 | Xenon | Xe | 131·3 |
| 7 | Nitrogen | N | 14·008 | 55 | Cæsium | Cs | 132·91 |
| 8 | Oxygen | O | 16·0000 | 56 | Barium | Ba | 137·36 |
| 9 | Fluorine | F | 19·00 | 57 | Lanthanum | La | 138·92 |
| 10 | Neon | Ne | 20·183 | 58 | Cerium | Ce | 140·13 |
| 11 | Sodium | Na | 22·997 | 59 | Praseodymium | Pr | 140·92 |
| 12 | Magnesium | Mg | 24·32 | 60 | Neodymium | Nd | 144·27 |
| 13 | Aluminium | Al | 26·97 | 61 | Promethium | Pm | [147] |
| 14 | Silicon | Si | 28·06 | 62 | Samarium | Sm | 150·43 |
| 15 | Phosphorus | P | 30·98 | 63 | Europium | Eu | 152·0 |
| 16 | Sulphur | S | 32·066 | 64 | Gadolinium | Gd | 156·91 |
| 17 | Chlorine | Cl | 35·457 | 65 | Terbium | Tb | 159·2 |
| 18 | Argon | A | 39·944 | 66 | Dysprosium | Dy | 162·46 |
| 19 | Potassium | K | 39·096 | 67 | Holmium | Ho | 164·94 |
| 20 | Calcium | Ca | 40·08 | 68 | Erbium | Er | 167·2 |
| 21 | Scandium | Sc | 45·10 | 69 | Thulium | Tm | 169·4 |
| 22 | Titanium | Ti | 47·90 | 70 | Ytterbium | Yb | 173·04 |
| 23 | Vanadium | V | 50·95 | 71 | Lutecium | Lu | 174·99 |
| 24 | Chromium | Cr | 52·01 | 72 | Hafnium | Hf | 178·6 |
| 25 | Manganese | Mn | 54·93 | 73 | Tantalum | Ta | 180·881 |
| 26 | Iron | Fe | 55·85 | 74 | Tungsten | W | 183·92 |
| 27 | Cobalt | Co | 58.94 | 75 | Rhenium | Re | 186·31 |
| 28 | Nickel | Ni | 58·69 | 76 | Osmium | Os | 190·2 |
| 29 | Copper | Cu | 63·54 | 77 | Iridium | Ir | 193·1 |
| 30 | Zinc | Zn | 65·38 | 78 | Platinum | Pt | 195·23 |
| 31 | Gallium | Ga | 69·72 | 79 | Gold | Au | 197·2 |
| 32 | Germanium | Ge | 72·60 | 80 | Mercury | Hg | 200·61 |
| 33 | Arsenic | As | 74·91 | 81 | Thallium | Tl | 204·39 |
| 34 | Selenium | Se | 78·96 | 82 | Lead | Pb | 207·21 |
| 35 | Bromine | Br | 79·916 | 83 | Bismuth | Bi | 209·00 |
| 36 | Krypton | Kr | 83·7 | 84 | Polonium | Po | 210 |
| 37 | Rubidium | Rb | 85·48 | 85 | Astatine | At | [210] |
| 38 | Strontium | Sr | 87·63 | 86 | Radon | Rn | 222 |
| 39 | Yttrium | Y | 88·92 | 87 | Francium | Fr | [223] |
| 40 | Zirconium | Zr | 91·22 | 88 | Radium | Ra | 226·05 |
| 41 | Niobium (Columbium) | Nb (Cb) | 92·91 | 89 | Actinium | Ac | — |
| | | | | 90 | Thorium | Th | 232·12 |
| 42 | Molybdenum | Mo | 95·95 | 91 | Protoactinium | Pa | 231 |
| 43 | Technetium | Tc | [99] | 92 | Uranium | U | 238·07 |
| 44 | Ruthenium | Ru | 101·7 | 93 | Neptunium | Np | [237] |
| 45 | Rhodium | Rh | 102·91 | 94 | Plutonium | Pv | [239] |
| 46 | Palladium | Pd | 106·7 | 95 | Americium | Am | [241] |
| 47 | Silver | Ag | 107·880 | 96 | Curium | Cm | [242] |
| 48 | Cadmium | Cd | 112·41 | | | | |

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